Origin of PL emission at 0.797 eV in near stoichiometric spray deposited CZTS thin films

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Abstract. Photoluminescence (PL) spectroscopy has been employed for analyzing defect levels in near stoichiometric Cu₂ZnSnS₄ (CZTS) thin films deposited using chemical spray pyrolysis (CSP) technique. An emission at 0.797 eV could be recorded at 15 K from the near stoichiometric CZTS thin films. This emission was persistent up to room temperature and could be identified as “donor to acceptor pair (DAP)” transition and also bears close connection with concentration of copper. Using temperature as well as excitation power dependent PL measurements and X-ray photoelectron spectroscopy (XPS) depth profile analysis, the emission at 0.797 eV could be identified as arising from transition between donor level (due to OSn defect) and acceptor level (created by CuZn defect).

1. Introduction

Research on CZTS, the economically viable and more eco friendly quaternary alternative to CIGS absorber, has gathered immense momentum and efficiency of photovoltaic device fabricated using CZTS has hit 8.4 % [1]. This material has favourable band gap in the range 1.4 -1.6 eV, high absorption coefficient and is composed of non-toxic earth abundant elements [2-4]. Another advantage of this material is that consumer friendly techniques can be successfully employed for its deposition, of which CSP is a scalable and easy to handle technique [5-9]. Works on this material are spreading in various directions because this is relatively a new comer in the PV industry and solid background check has to be done. This material has properties that seem to be extremely good from all perspectives and to improve performance of the device based on CZTS, a thorough analysis of the problems associated with CZTS is essential. Defects in a material generally tend to deteriorate performance of any device fabricated using the material but in some cases, defects turn out to be useful too. Identifying defects itself is a study on its own and first principle calculations and theoretical investigations have been carried out on CZTS which provide insight in to the most probable defects and their locations within the band gap [10-12]. Over the past few years, defect analysis using Raman & PL spectroscopy on this material has also been reported by some groups [13-18]. In most of the reports based on PL, they have discussed on emissions close to the band gap [13, 14, 20]. The reports are mainly on CZTS bulk monograins or polycrystalline CZTS grown through vacuum based techniques. In this paper, the authors have attempted to reveal origin of ‘close-to-midgap’ emission at 0.797eV, in spray deposited (nearly stoichiometric) CZTS thin films.
2. Experimental Techniques
Stoichiometric CZTS thin films [sample A] were prepared using chemical spray pyrolysis (CSP) technique on soda lime glass substrates, maintained at temperature of 350 °C. Details regarding film deposition and characterization have been reported elsewhere [19]. In the present report, focus is only on defect analysis using PL and for PL studies, the sample was excited with 632.8 nm line of He-Ne laser (Melles Griot; 15 mW) and 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 on the cold finger of a closed cycle liquid helium cryostat (Janis Research Inc.). X-Ray Photoelectron spectroscopy (XPS) measurements were done using ULVAC- VHI unit (Model- ESCA 5600 CIM) employing argon ion sputtering.

3. Results and Discussion
Radiative transitions can occur in semiconductors via ‘band to band’ recombination or through ‘defect-assisted’ recombination. PL spectroscopy has been used to unearth recombination mechanism. CZTS being a quaternary compound semiconductor, defects that are likely to arise under any deposition condition are numerous. Along with the vacancies and interstitials of Cu, Zn, Sn and S, intrinsic point defects such as CuSn, CuZn etc also arise due to antisite substitutions [20]. Figure 1 is the PL spectrum recorded from sample A at 15 K.

![Figure 1: PL spectrum of sample A](image)

PL spectrum comprises of just a single peak centered at 0.797 eV. No band to band emissions could be recorded from sample A. Since the emission is lower than the band gap value of ~1.45 eV, mechanism for this emission should be something other than band to band recombination. Dependence of PL intensity on excitation power is given by

\[ I \propto P^\gamma \]

where \( I \) is PL intensity, \( P \) is excitation power and \( \gamma \) is an exponent. Generally, \( \gamma \leq 1 \) for donor to acceptor (DAP) transition and free-to bound transition respectively and \( 1< \gamma <2 \) for excitonic transitions. Variation of PL intensity from sample A for different excitation powers was studied. Figure 2 is a log-log plot of PL intensity vs excitation power.
Figure 2: Log-log plot of PL intensity vs excitation power

Value of the exponent $\gamma$ was obtained to be 0.8, indicating that the transition is clearly DAP type. Another feature of DAP transition is blue shift in peak energy position with excitation power. The peak energy (of the emission at 0.797 eV) has blue shifted by few meV with excitation power (shown in Figure 3) which again confirms that the transition is DAP type.

Figure 3: Variation of PL peak energy with log (excitation power)

Temperature dependence of PL emission at 0.797 eV was monitored and activation energies of defects involved were calculated. Figure 4 shows the Arrhenius plot [log (PL intensity) vs 1000/T] for the emission at 0.797 eV from sample A.

Figure 4: Log (PL intensity) vs 1000/T plot obtained for sample A

The activation energy can be obtained from the plot by fitting the experimental curve with the relation
\[ I(T) = I(0)/[1 + Ce^{-\Delta E/kT}] \]

where \( I(T) \) and \( I(0) \) are PL emission intensities at temperature \( T \) and 0 K respectively. \( C \) is a constant related to capture cross section and \( \Delta E \) is activation energy. Activation energy of \( \sim 0.12 \) eV was obtained. Previous reports on first principle calculations predict occurrence of prominent acceptor at 0.12 eV above valence band maximum (VBM) which is attributed to Cu\(_{zn}\) defect; this is one of the predominant intrinsic defects with very low formation energy [12, 21]. Cu\(_{zn}\) antisite defect is thermodynamically the most stable defect and has negative formation energy for allowed chemical potential range. This defect accounts for the p-type conductivity in CZTS. Sample A is p-type and low resistive [19] and obtained activation energy value coincided with the reported value. Thus the level at 0.12 eV was attributed to Cu\(_{zn}\) antisite defect. Band gap of sample A is \( \sim 1.45 \) eV and since position of acceptor level is \( \sim 0.12 \) eV from VBM, it becomes obvious that emission at 0.797 eV was absent in samples B. This might be because oxygen related defects were removed on vacuum annealing. The only way to confirm whether the donor is created due to oxygen occupying the lattice sites of tin viz., O\(_{Sn}\), is to purposely increase the tin content in the sample. By doing so the lattice sites expected to be occupied by tin shall be filled and oxygen will be left with no chance to occupy tin sites and the formation of the defect O\(_{Sn}\) will be highly unlikely. Thus the expectation was that the emission would disappear when tin content is purposefully increased. Another set of samples C were prepared, by increasing the Sn content in the stoichiometric sample from 1 to 1.3 and PL spectrum was recorded. As expected, the emission was absent in sample C. PL spectra of samples B and C along with that obtained for sample A shown in Figure 5.

![Figure 5: PL spectra of samples A, B and C](image)

To confirm that excess tin restricts oxygen incorporation XPS depth profile analysis was done on samples A [stoichiometric] and C [Sn excess]. Generally from XPS measurements information regarding the chemical state and binding energies are obtained. Binding energy values indicate formation of CZTS in both samples A and C. Depth profile of atomic concentration of various elements from surface to the depth of the sample was also done. In order to get information from the depth, surface layers were etched out by sputtering and XPS measurements from each layer were taken. Graph is then plotted between atomic concentration and sputter time. Sputter time \( t=0 \) min implies the surface of the sample and with progress in sputter time information from the depth of the sample is obtained.
Fig 6 (a) is the atomic concentration vs sputter time graph of sample A where it is clear that oxygen is present in the sample as a contaminant. Fig 6 (b) is a similar plot for sample C which clearly indicates excess Sn is successful in restricting oxygen incorporation.

![Atomic concentration vs sputter time plot of (a) sample A (b) sample C.](image)

Thus from XPS results, midgap level can be attributed to O\textsubscript{Sn} defect. Thus the recorded emission at 0.797eV arises due to recombination between a close to midgap defect due to O\textsubscript{Sn} and an acceptor created by Cu\textsubscript{Zn}.

**Conclusion**

In the report the mechanism of PL at emission at 0.797 eV in near stoichiometric spray deposited CZTS emission was studied. It was shown that the emission pyrolysed CZTS thin films at 0.797eV arises due to recombination between a close to midgap defect due to O\textsubscript{Sn} and an acceptor created by Cu\textsubscript{Zn}. In thin films high aspect ratio can also effects on all PL emission mechanisms [23]. For further deeper understanding the nature of the mechanism PL emission in thin films the future work can be related to the study of possible influence of aspect ratio and geometric factor on the mechanism of PL emission. Such study can be carried out though comparison of PL emission of thin CZTS films, obtained in this report, bulk samples and nano-CZTS materials, like, nanowire array [23]. It was shown for some application [25] that nanodevices based on individual nanowires is excellent tool for fundamental study of the correlation between functional properties of the device and the structure and composition of the material. Thus, study of PL emission in individual CZTS-nanowires is important for the understanding of the mechanism of PL emission at nanoscale [24]. To overcome difficulties in the investigation of PL from single CZTS nanowire it is possible to use nanomanipulation technology [25]. This nanomanipulation technology allow selection, removing from substrate, pick up and place of such individual nanowires on the special substrate for further investigation, for example using STED microscopy.

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