Room Temperature Photoluminescence Surface Mapping

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Abstract: Photoluminescence mapping system using tip illumination/tip collection and tip illumination/far field collection has been described and it is found that the latter collection mode is better suited for luminescence signal collection. Emphasis has been laid on the information that can be gained from the spatial measurements of luminescence emission intensity at single wavelength (topography) and different wavelengths. The results of measurement on CuInS2 thin films prepared using spray pyrolysis technique are presented. Characterization of the defects in the film has been achieved. The effect of non-uniform film deposition on the luminescence has been realized.

1. Introduction
More than 95% of the energy emitted by the sun is concentrated in a narrow span of 240nm-2500nm, peaking at green. CuInS2 thin films have an edge over all other photovoltaic material because it has an optimal band gap of \( \approx 1.5 \text{eV} \), which is necessary for maximum absorption of the solar spectrum. There are several reports on synthesizing CuInS2 using different techniques for fabricating solar cells and some of the cells exhibited efficiency of the order of 12% [1-5]. Our group recently reported an all sprayed CuInS2/In2S3 thin film solar cell with an efficiency of 9.5% [6]. However we observed that the efficiency was not uniform over the entire area of the cell. In order to understand the reason for this spatial variation, we performed a room temperature photoluminescence surface mapping study of the samples.

Defects in a compound semiconductor like CuInS2 are mainly due to variation in stoichiometry rather than due to external doping. PL emission from the sample is the signature of defect/impurities in the sample. The peak intensity variation can be related to variations in layer thickness and/or the number of non-radiative recombination centers i.e., the quality of the material [7]. Jeon et all [8] showed that bright and dark regions of a surface map did not show any shift in peak position suggesting that the origin of the spatial variation of PL intensity was due to variation of density of defects which act as non radiative recombination centers.

In this paper we report the results of room temperature PL surface mapping done using two techniques viz: tip illumination/tip collection-technique ‘A’ and tip illumination/far field collection-technique ‘B’ on CuInS2 thin films, prepared using spray pyrolysis. In the region of scan we could find a decrease in the PL peak intensity and also a shift in PL peak wavelength.

2. Experiment
The experimental arrangement for photoluminescence in the technique A is shown in fig 1(A). The sample was mounted on an XYZ translator. He-Ne (632.5nm) laser was used as the excitation source. The beam was coupled into a bifurcated/ split optical fiber by using a lens and an SMA adaptor. The optical fiber was brought to an
optimal distance from the sample where maximum signal strength was detected. The split fiber had five illumination and one collection channel. The collection channel was fed into the spectrophotometer (USB 2000, Ocean optics Custom made) by using SMA adaptors. A computer controlled the spectrophotometer, where from we could command, to either scan the entire wavelength spectrum from 350-900nm or scan at a constant wavelength with a time base.

Schematic for technique A and B are given in figure 1 (B) and (C) respectively. In technique B the split fiber was replaced with a single fiber for illumination, and collection lens are used to couple the emission from the sample to the spectrophotometer. The scan was done over 1cm² area of the sample, by moving the translator in steps of 1000µm. A total of 100 points were scanned and a 10 by 10 square matrix was set up for obtaining the surface contour maps.

3. Results and Discussion
The PL emission spectrum of CuInS₂ at room temperature was obtained as shown in fig 2. The spectrum peaked at 835nm with a FWHM of 12meV. The emission was lower than the reported band gap value 1.55eV of CuInS₂ [9] by 63 meV, which was close to the activation energy of In [10]. Hence we assumed that this emission was due to transition from the Inₐ donor level to the valence band. The spatial variation in its intensity and FWHM is shown in fig 2b.

The signal intensity was converted into a false color image, where color was a function of signal intensity. A comparison of the topography obtained by the two operational modes of PL measurements is shown in fig 3. The color palette used followed the spectrum (BGYOR) with the signal intensity increasing from blue to red. The signal intensity collected by the technique B was nearly three times the intensity collected by technique A. This improvement in signal collection was in direct agreement with earlier reports made on use of tip illumination/far
field collection for PL measurements [11]. The localized excitation caused increase in PL signal. More over collection optics with high numerical aperture lead to high collection efficiency. For technique A, the limited throughput for excitation and collection, lead to small optical signals.

The edges of both the graphs are of same nature with the signal strength being weak. The intensity was high for both the modes in the same region (i.e. in the central region) indicating that the specific region was uniform in defect density or else the intensity profile would have been different. This region is the most defective causing maximum emission from the defect to the valence band. Comparison of figure 2 with figure 1(b) indicated that the larger FWHM was observed for darker regions than in brighter regions. This correlation between the PL intensity and FWHM indicated that origin of the non-uniformity of light emission might be due to non-uniform distribution of the defect/structural imperfections.

![Figure 3: Single wavelength Contour map of (A) tip illumination/far field collection mode (B) tip illumination/tip collection mode. Here change in colour represents change in peak intensity as shown in color bar on the right](image)

The decrease in signal strength observed in Fig 3 towards the edge may be due to the shift in the peak wavelength resulting from the presence of another type of defect. Fig 4 shows the plot of peak wavelength as a function of spatial position using the technique B. In this figure, the color corresponded to the wavelength shown in the color bar on the right side of the figure. It is very clear that the peak shifted to higher wavelengths near the edges. In the single wavelength scan, this shift contributes to the decrease in PL intensity as seen in figure 2. The peak wavelength shifted to 852nm from 835nm. This is lower than the band gap by 92meV and corresponds to the activation energy of sulphur vacancy (V_S -90meV) level [9].

![Figure 4: Peak wavelength analysis of CuInS_2. Here change in color reflects change in peak wavelength as shown in the color bar on the right.](image)

It might be assumed that such variation in emission wavelength was arising from the non-uniformity of the film i.e. the region having PL emission of 835nm was having defect of In, while the region having PL emission of 852nm was having higher density of V_S. Probably due to this non-uniformity of the defect distribution in the film, p-n junctions in different regions were also not functioning uniformly. The junction efficiencies are known
to be poor for samples, which are In rich and/or sulphur deficient. The most efficient solar cells have been achieved on Cu-rich films. From this study, using PL, we were able to identify the origin of non-uniformity causing spatial variation in cell performance.

4. Conclusions
The data presented indicate that technique B was a better tool than technique A for photoluminescence studies. The spatial mapping of parameters such as peak wavelength and peak intensity provided information about the sample that was vital in evaluating deposition technique, and the uniformity of deposited layers. They also indicated that a single point measurement of a spectral parameter is not enough to completely evaluate a sample. In our samples we detected a spatial distribution of the Indium interstitial (In\(_i\)) and sulphur vacancy (V\(_S\)) levels. The spatial decrease in 835nm PL intensity was due to the shift of the emission peak to the 852nm. The shift in the emission peak was due to non-uniform distribution of the two defect levels in the material.

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