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# Characterization of stepwise flash evaporated $CuIn_3Se_5$ films

P. Malar, S. Kasiviswanathan*

*Department of Physics, Indian Institute of Technology-Madras, Chennai 600 036, India*

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**Abstract**

$CuIn_3Se_5$ thin films were grown by stepwise flash evaporation from the polycrystalline powder source. Bulk $CuIn_3Se_5$ was synthesized by melt-quench technique, starting from the stoichiometric mixture of constituent elements. Phase purity of the synthesized material was confirmed by powder X-ray diffraction. Structural investigations by transmission electron microscopy (TEM) show that the films grown at 370 K and above were polycrystalline in nature. Compositional analysis by Rutherford backscattering spectrometry (RBS) revealed that the films have near stoichiometric composition. Analysis of optical transmittance data yielded a band gap value of $\sim 1.26 \pm 0.02$ eV.


*Keywords:* Ordered defect compounds; XRD; TEM; RBS

## 1. Introduction

$CuIn_3Se_5$ is a ternary semiconducting compound belonging to the $\beta$-phase of the Cu–In–Se system [1–3]. It is one of the In-rich phases, located on the ($Cu_2Se$)–($In_2Se_3$) quasi-binary tie-line. The structural tolerance to off-stoichiometry of the $\alpha$-phase (chalcopyrite $CuInSe_2$) at the extreme limits, beyond 47.5 to 55.0 mol% of $In_2Se_3$, gives compounds with different compositions such as $CuIn_5Se_8$, $CuIn_3Se_5$ and $Cu_3In_5Se_9$ [4,5]. Existence of off-stoichiometric compounds on the In-rich side of $Cu_2Se$–$In_2Se_3$ has been attributed to the ordering of the neutral defect pair

*Corresponding author. Fax: 91-44-22570509.
*E-mail address:* kasi@iitm.ac.in (S. Kasiviswanathan).

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($2V_{Cu}^{-}+In_{Cu}^{2+}$) in $CuInSe_2$ [6]. This defect pair has unusually low formation energy and therefore, stabilization of these Cu-poor phases is energetically favorable [6]. Consequently, these compounds are called ordered defect compounds (ODCs) or ordered vacancy compounds (OVCs). $CuIn_3Se_5$ is often detected as a segregated secondary phase at the surface of the In-rich $CuInSe_2$ thin films [7]. Recently, the ODCs related to the other compounds of the I–III–$VI_2$ family of chalcopyrite semiconductors are also established and their structural, optical and electrical properties are reported [8,9].

The structural studies on ODCs show that the X-ray diffraction (XRD) pattern of $CuIn_3Se_5$ is very similar to that of $CuInSe_2$ except for a few additional reflections, which distinguish it from $CuInSe_2$ [1]. The reflections due to (0 0 2), (1 1 0), (2 0 0), (2 0 2) and (1 1 4) planes are the characteristic lines of ODCs and do not obey the extinction conditions for the space group $I\bar{4}2d$ of the chalcopyrite structure. Therefore, $CuIn_3Se_5$ is expected to have a crystal structure different from that of the chalcopyrite structure. Honle et al. [10] have proposed a space group $P\bar{4}2c$ on the basis of refinement of crystallographic data of Cu-poor $\beta$-phase with a composition of $Cu_{0.39}In_{1.20}Se_{2.00}$. Neumann et al. [11] have found their results on TEM studies of $CuIn_3Se_5$ single crystals to agree well with that of the structure model proposed by Honle et al. [10]. Hanada et al. [12] on the other hand, have proposed the space group $I\bar{4}2m$, based on convergent beam electron diffraction studies of $CuIn_3Se_5$. Although, a consensus has not yet been established on the type of space group, several reports are available on the growth and characterization of single crystals as well as thin films of $CuIn_3Se_5$. The fundamental absorption edge in $CuIn_3Se_5$ has been reported to be direct in nature. The reported values for band gap range from 1.20 to 1.31 eV [7,13,14], which are distinctly different from those of $CuInSe_2$ (0.9–1.04 eV). The higher band gap of $CuIn_3Se_5$ compared to $CuInSe_2$ is owing to the reduced p–d hybridization and the consequent increase in the band edge separation, caused by Cu-vacancies [15,16].

$CuIn_3Se_5$ with its n-type conductivity and a higher band gap value than $CuInSe_2$ can readily form a heterojunction with p-type $CuInSe_2$. In fact, a thin segregated layer of $CuIn_3Se_5$ on $CuInSe_2$ has been shown to increase significantly the efficiency of $CuInSe_2$ based solar cells [7]. In such heterostructures, the key factors that decide the optimum device performance are the compositional uniformity and phase purity of the different layers that form the heterostructures. Therefore, it is of importance to investigate in detail the growth and characterization of ODCs, with respect to deposition parameters and growth techniques.

In this paper, we report the results on growth of $CuIn_3Se_5$ thin films by stepwise flash evaporation [17–19] and subsequent characterization by TEM, RBS and optical absorption. Various techniques such as molecular beam epitaxy [20,21], RF sputtering [22], hybrid sputtering and evaporation [23], three source co-evaporation [24] and flash evaporation [25] have been used for the deposition of $CuIn_3Se_5$ films. Of these, flash evaporation is an inexpensive technique and is used for growing thin films of compounds and multicomponent alloys. However, splluttering of the source powder during evaporation causes wastage of material, in addition to compositional non-uniformity and poor reproducibility. We have deposited thin films of $CuIn_3Se_5$