



Review

Electrical conductivity tuning and valence band splitting studies in Copper Gallium Selenide thin films

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ABSTRACT

Copper gallium selenide (CGS) semiconductor thin films are suitable for various optoelectronic devices due to their stoichiometry dependent properties. Tuning of electrical conductivity (0.5–90 S/cm) by compositional variations of CGS thin films prepared by reactive evaporation of the three elements under vacuum is presented here. This p-type absorber material withstands its conductivity type over the entire range of compositional variation. The structure, morphology, elemental composition, chemical states, electrical and optical properties of the thin films are characterized using techniques like X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, UV–visible absorption spectroscopy and Hall effect measurements. Optical studies of the films reveal a three-fold absorption from which crystal field splitting ~0.06 eV and spin orbit splitting ~0.09–0.17 eV are determined. The optical fundamental absorption edges of the films vary from 1.6 to 1.67 eV.

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1. Introduction

The I-III-VI₂ chalcopyrites are useful in improvising a variety of devices like photovoltaic solar cells, visible and infra-red light emitting diodes, infra-red detectors, optical parametric oscillators,

up convertors, far infra-red generators, photo electrochemical water splitting, thermo electric devices, topological insulators etc. [1–10]. The properties which render them conducive for their wide use include their semiconducting nature with high optical absorption coefficient (10^4 – 10^5 cm⁻¹), near optimum band gap energy (~1.1–2 eV) and the presence of band edges that are tunable by composition [3,5,6,9,11–13]. Of the chalcopyrite compounds, the material properties of ternary copper indium selenide (CIS) and quaternary copper indium gallium selenide (CIGS) are extensively

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studied due to their wide application as absorber layers in solar cells. The studies on CuGaSe₂ (CGS) are comparatively fewer and the performance efficiency of CGS solar cell is currently stationed in the range of 10% [11]. The observed low conductivity $\sim 10^{-5}$ to 0.7 S/cm for the compound [4,13] is identified as one of the limiting factors in its applications. To circumvent its limitations for device applications, it is imperative to explore in detail the material properties of the compound. Various studies have suggested that CGS exhibits p-type conductivity, irrespective of the variations in its stoichiometry which is accounted for by the doping-pinning rule [4]. The binaries of CGS also exhibit p-type conductivity [14]. The present study aims at the preparation of CGS thin films of composition varying from far off stoichiometric to stoichiometric with both Cu rich (Cu/Ga~1.64) and Ga rich (Cu/Ga~ 0.67) off stoichiometry to investigate the possibility of tuning the conductivity and optical band gap through composition variation. Even though several techniques are employed for growing CGS absorber layers such as Liquid Phase Epitaxy, Metal-Organic Vapor Phase Epitaxy, Molecular Beam Epitaxy and Halogen Transport Method [15], a grouping based on electrical conductivity by effecting a wide range of stoichiometric variations has not been reported so far. The present study convincingly reveals the scope of tuning the electrical conductivity and band gap of this absorber material while maintaining the p-type conductivity. The paper also discusses the valence band splitting due to spin-orbit and crystal field effect that is observed in near stoichiometric CGS samples.

2. Experimental

CGS thin films are deposited on soda lime glass substrates kept at a temperature of 523 ± 5 K, by reactive evaporation of Cu, Ga and Se of purity 99.999%, in a vacuum coating unit maintained at a pressure of $\approx 10^{-5}$ Torr using modified form of Gunther's three temperature method [16,17]. The compositional variation is achieved by control of flux of each source. For this, simultaneous and independent evaporation by resistive heating is done for Cu and Ga from individual molybdenum boats and for Se from a glass crucible kept in a molybdenum basket. The impingement rate of each element has first been determined under fixed vacuum conditions, substrate temperature and source current. Then by using pre-determined quantities of each element (Cu weight varying from 0.04 to 0.06 g and Ga weight from 0.05 to 0.07 g), the flux of each element has been varied to obtain films of different compositions [17,18]. However, since the reaction in this technique is happening at the substrate, the compositions of the films have been determined by Energy Dispersive Analysis of X-rays (EDAX) and X-ray Photoelectron Spectroscopy (XPS) before grouping the samples. The preliminary structural characterizations are done by X-ray diffraction (XRD) using a Bruker AXS D8 Advance X-ray diffractometer with CuK α 1 as the source radiation ($\lambda = 1.5404$ Å) and Raman spectra using a Micro Raman system JobinYvon Horiba LABRAM-HR visible (400–1100 nm). EDAX measurements are done using JEOL JED-2300 6490(LA) and XPS using XPS Thermo Scientific K-Alpha equipped with monochromatized Al-K α radiation ($E = 1486.68$ eV) for compositional analysis and Scanning Electron Microscopy (SEM) by JEOL JED – 2300 for morphological studies. Optical absorbance spectra are taken using Hitachi UV–Vis–NIR spectrophotometer. The room temperature and high temperature conductivity has been measured using Keithley 2611A source meter, using silver paste for ohmic contact. Hall Effect measurements are done by applying a magnetic field of 0.54 T and measuring the voltage for different currents by four probe method employing Vander Pau technique using Ecopia Hall effect measurement system (HMS 3000).

3. Results and discussion

3.1. Electrical analysis

The electrical conductivity(σ) studies at room temperature (~ 300 K) on CGS samples of different compositions are done by grouping the samples based primarily on anion/cation ratio (Se/(Cu + Ga)) which is kept between 0.7 and 1.44. For this, compositions of all the samples are determined using EDAX and XPS. The samples are divided into two groups; those having Se/(Cu + Ga) value greater than 1 and less than 1, with each group having two more divisions where Cu/Ga value (kept between 0.67 and 1.6) is greater than 1 and less than 1 as shown in the schematic division Fig. 1. It is noted that for all CGS samples p-type σ is invariably observed in agreement with that reported by various authors [4,13]. The room temperature σ of all the stoichiometric films is found to be low of the order of 0.5–0.7 S cm^{-1} . It is evident from Fig. 1 that the room temperature σ is greatly influenced by the Cu/Ga ratio in Se-rich samples (Group I) where it ranges from 5 to 30 S/cm while no predominant effect of Cu/Ga is observed in Se-deficient samples (Group II) where it varies from 30 to 90 S/cm. To be more specific, the samples (Ia) coming in the Se rich group I with Cu/Ga>1 show two orders of magnitude increase in electrical conductivity (~ 20 – 30 S/cm) when compared with stoichiometric samples whereas that in group (Ib) with Cu/Ga<1 show moderate conductivity (one order of magnitude higher than in stoichiometric), while in both cases p-type nature is invariably reproduced. A similar observation is reported in CuInSe₂ thin films by Noufi et al., though in their case in indium rich films n-type conductivity is also found as a possibility [19]. This difference aligns with the observation that indium selenide usually manifests n-type conductivity [20] while Gallium selenide is invariably p-type [21]. For the films in Se deficient Group II, there is an enhancement of two orders of magnitude in σ when compared with the stoichiometric films. The highest σ at room temperature ~ 90 S/cm is observed for those films in IIc where the cation content is maximum (ranging from 30 to 90 S/cm for deviation of Se/(Cu + Ga) ratio from 0.96 to 0.7). This suggests a tendency for increase in room temperature σ with decrease in anion/cation ratio. Here also no switching of electrical conductivity from p-type to n-type is observed. Based on these observations the room temperature electrical conductivities are marked as follows.

A better understanding of electrical conductivity tuning is obtained by carrier concentration and mobility determination from Hall effect measurements at room temperature (~ 300 K). The parameters depicted in Table 1 indicate that an increase in hole concentration by about two orders of magnitude compared to that in stoichiometric samples is behind the improved conductivity of group II samples compared to latter. The activation energy $E_a \sim 97$ meV in stoichiometric films indicates Se interstitials, which aligns with the anion/cation ratio ~ 1.03 in the stoichiometric samples. The probability defect in the Group II samples is Se vacancies, as can be interpreted based on the activation energy from $1000/T$ versus $\ln \sigma$ graphs fits (Fig. 2), since both IIc and IIc give the same activation energy (~ 25 meV) indicative of identical defects in both Cu rich and Ga rich films. This observation that the material remains p-type with Se vacancies is in consonance with Noufi et al.'s observation in Se deficient CuInSe₂ samples where the p-type behavior is accounted for by conservation of charge neutrality with the reduction of In^{3+} to In^{2+} or In^{1+} which creates acceptor states [19]. A similar behavior can be suggested in the present case where instead of In in CIS, Ga^{3+} reduction can happen. It is seen from σ of group II samples in Table 1 that increase in Cu vacancies in Se deficient samples increases their p-type behavior. This is also in tune with Noufi et al.'s observation though opposing the speculations for single crystals of chalcopyrites [19]. The slightly deeper

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