CHARACTERISTICS OF PULSE PLATED COPPER GALLIUM TELLURIDE FILMS

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Abstract

Copper Gallium Telluride films were deposited for the first time by the pulse electro- deposition technique at different duty cycles in the range of 6–50% at room temperature and at a constant potential of -0.78 V(SCE). The films exhibited single phase copper gallium telluride. The grain size increased with increase of duty cycle. Optical band gap of the films varied in the range of 1.235-1.25eV. Atomic force microscopy studies indicated that the grain size and surface roughness vary from 20 nm to 35 nm and 0.8 nm to 1.2 nm, respectively with increase of duty cycle. Capacitance voltage measurements indicated the films to exhibit p-type behavior. The flat band potential was 0.72 V (SCE) and carrier density was in the range of 10^{16} cm^{3}.

Key words

Thin films, Pulse electrodeposit, 1–III–VI_2 semiconductors, and chalcopyrite.

Introduction

Cu–III–VI_2 chalcopyrite semiconductors are feasible candidates for application as photo detectors [1], photo- voltaic cells [2] and light- emitting diodes [3]. Among Cu-based chalcopyrite, a high efficiency of 19.9% has been achieved for Cu(In,Ga)Se_2 (CIGS) based-thin film solar cells with small areas (1 cm^2) [4]. There has been increasing interest in the material properties of I-III-VI, compounds whose energy gap lies between 0.9 and 3.5 eV, as they exhibit great potential for the manufacture of electro-optical devices [5]. Though I-III-Se_2 compounds have received much attention in recent years, there are relatively fewer studies on I-III-Te_2 . Earlier reports on $CuGaTe_2$ show a direct band gap semiconductor with an energy gap of 1.23 eV. Bulk $CuGaTe_2$ exhibited p-type conductivity due to shallow acceptors [6] with a hole concentration of about 10^{18} cm^{-3} at room temperature [7].$CuGaTe_2$ films have been deposited by flash evaporation [8], electrodeposition [9], pulse laser deposition [10] etc. In this work, the pulse electrode position technique was employed for the first time [11] to deposit $CuGaTe_2$ (CGT) films for applications of solar cells.

Experimental methods

Copper Gallium telluride were deposited on tin oxide coated conducting glass substrates at room temperature and at a deposition potential of -0.78 V Vs Saturated Calomel Electrode (SCE) by pulse electrodeposition method[12]. The total deposition time was 60 min. the precursors used were Analar grade 0.25 mM $CuCl_2$, 0.25 mM $GaCl_3$, 0.25 $InCl_3$ and 100 mM TeO_2.

Thickness of the films estimated by Mitutoyo surface profilometer, it varied from 0.7㎜ cycle. The films were characterized by Xpert panalytical x-ray diffraction unit with Cu ka radiation. Optical measurements were recorded using a Hitachi UV–Vis-IR spectrophotometer. Surface morphology of the films was studied by molecular imaging atomic force microscope.

3. Results and discussion

Fig.1 depicts the XRD patterns of the films deposited at different duty cycles. The films were polycrystalline with peaks corresponding to (112), (220) and (312) planes of crystalline $CuGaTe_2$ at approximately 2θ= 24.20˚, 40.21˚ and 47.29˚, respectively matches with (JCPDS card No.10–0421). As the duty cycle increased, the intensity of the peaks increased and the width of the peak decreased. The crystallite size was estimated from the Scherrer's equation to be 30nm-70nm

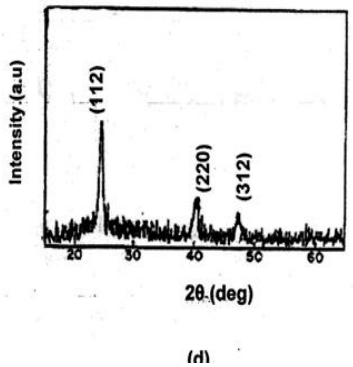

Fig 1

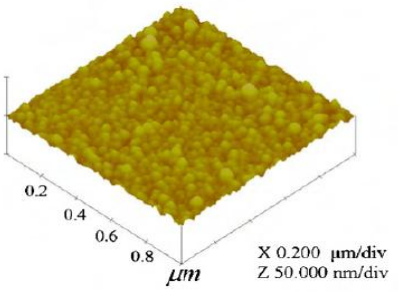

Fig 2

Fig 1- X-Ray diffraction pattern of $CuGaTe_2$ deposited at 50% duty cycles

Fig 2 -Atomic force micrographs of Copper Gallium Telluride deposited at 50% duty cycles

The obtained stoichiometric composition from EDS study is close to the ideal composition of $CuGaTe_2$.The quantified stoichiometric composition is Cu (28.95 at %), Ga (27.80 at %) and Te (43.25 at %). For films deposited at lower duty cycles a slight excess of Cu is observed. For the films deposited at 6% duty cycle, the composition was Cu (26.54 at %), Ga (25.56 at %) and Te (47.90 at

%).

Atomic force microscopy studies were made on the films deposited at 50% duty cycles. Fig.2 shows the Atomic force microscopy images. The grain size and surface roughness vary from 20` nm to 35 nm and 0.8 nm to 1.2nm, respectively.

Optical absorption studies were made on the films deposited at different duty cycles. The films exhibited a high absorption co-efficient of the order of 10^4 cm^1. A plot of $(\alpha h\upsilon)^2$ against hυ, as indicated in Fig. 3, exhibited linear behavior near the band edge, the band gap of the deposited material was determined to be in the range of 1.235-1.25 eV. The band gap was found to slightly increase with decrease of duty cycle, due to the small grain size. The band gap of $CuGaTe_2$ in thin film prepared by other technique was reported to be 1.21-1.24 eV [13]. The band gap of thin films obtained in the present work is in fair agreement with this value.

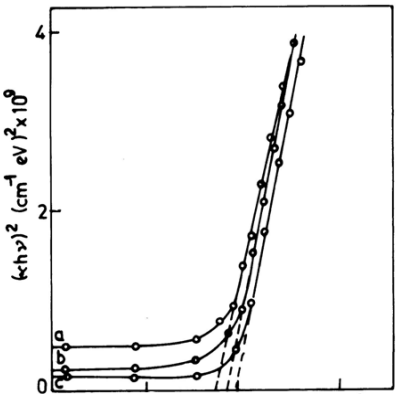

Fig 3$(\alpha h\upsilon)^2$ Vs hυ plot of $CuGaTe_2$

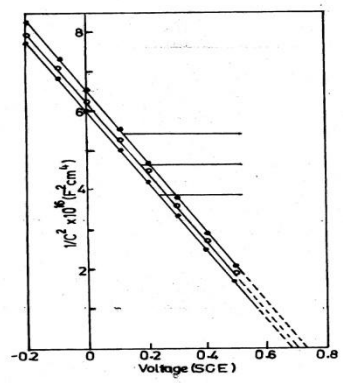

Fig.4 - Mott Schottky plots of $CuGaTe_2$ films deposited at different duty cycles (a) 15 % (b) 33 % (c) 50 %

. Fig. 4 shows the Mott-Schottky plot of the $CuGaTe_2$ films deposited at different duty cycles. 1 M $Na_2(SO_4)_2$ blocking electrolyte was used, the AC frequency was 10 kHz. Linear plots were obtained. The nature of the plot with negative slope indicates p-type behavior. Vfb of 0.68 - 0.72 V (SCE) and a carrier density in the range of $2.5 * 10^{16}$ cm ^{3} were obtained.

Resistivity of the films deposited at different duty cycles was measured by the two probe resistivity technique. Evaporated gold dot contact at the center of the top of the film served as one contact, while the conducting glass substrate served as the other contact. The resistivity of the films decreased from 40 Ω cm to 20.0Ω cm with increase of duty cycle. The resistivity decreases for lower duty cycles since the Cu/In ratio is greater than 1 for the films deposited at duty cycles lower than 50% (supported by the EDS data).

Table 1 Variation of resistivity with duty cycle.

Duty cycle (%)	Resistivity (ohm cm)
6	40
9	36
15	29
33	22
50	20

Using the value of carrier density obtained from the M-S studies and the resistivity value of 40 Ω cm for the films deposited at 50% duty cycle, a

value of 20 $cm^2V^{-1}S^{-1}$ was obtained for the mobility. The resistivity values for the films deposited at different duty cycles are shown in Table 1.The value of resistivity is higher than earlier report.

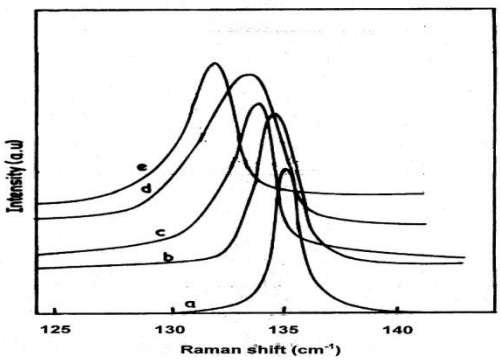

Fig.5– Raman spectra of CGT films deposited at different duty cycles 50 % (b) 33 % (c) 15 % (d) 9 % (e) 6 %

Fig 5 shows the Raman spectra of $CuGaTe_2$ films deposited at different duty cycles. It can be observed that A1 mode shifts to higher frequencies with increase of duty cycle. The width of the peak also decreases as the duty cycle increases.

4 Conclusions

The results of this work clearly points to the possibility of depositing single phase nano crystalline $CuGaTe_2$ films. Films with band gap in the range of 1.235 – 1.25 eV can be obtained. P-Type films with carrier density in the range of $2.5*10^{16}cm^{-3}$ can be obtained. So this work shows $CuGaTe_2$ can be used as a better alternate for $CuGaSe_2$ in solar cell applications.

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