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FTIR and Optical Absorption Studies of $CuSe_2$Thin Film

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Abstract

Polycrystalline thin films of $CuInSe_2$ have been prepared by Chemical Spray Pyrolysis technique. The films were obtained onto glass substrates by spraying the precursor solutions of A.R. purity. The preparative parameters, equimolar (0.05 M) concentration solution, 5 ml / min Spray rate, distance between nozzle to substrate (30cm) were optimized to obtain good quality thin films. FTIR and optical absorption studies of $CuSe_2$Thin Film were investigated. The as - deposited films were characterized for physical structure. The morphology of CuSe has been studied with scanning electron microscope (SEM). The optical studies revealed that the absorption coefficient is high (10^{-4} to 10^{-5} cm^{-1}) and the energy gap decreased continuously from 2.13 eV. The electrical transport studies for these films were also examined. The different transport characteristics of the films have also been determined. Thermo power measurements showed that the samples are n-type.

Keywords: Chemical Spray Pyrolysis, $CuSe_2$, thin films, thermo power.

1. Introduction

Substantial progress has been made in polycrystalline thin-film photovoltaics in the last few years [1]. All the thin-film deposition techniques used for the fabrication of high-efficiency CIS cells are costly and require sophisticated instruments. A low-cost process for the deposition of CIS thin-film layers is yet to be developed. This has been identified as one of the important issues related to CIS technologies that has to be addressed urgently [1]. All the thin-film deposition techniques, chemical spray pyrolysis technique (CSP) is the simplest and capable of large area fabrication at a low cost. The process has the added advantages that material wastage is minimum. This technique has been used for quite some time for the preparation of many binary semiconductors like CdS [2-5]. Its potential has not been fully utilized in developing ternary compound semiconductors probably because of the difficulty in controlling the process to get good quality films in a reproducible way. We developed this process to deposit solar-grade thin films on glass substrates. It was fabricated, with good photovoltaic activity [6]. In this paper, we present the detailed characterization of the $CuSe_2$ thin films related to FTIR and optical absorption study.

2. Experimental procedure for the deposition of $CuSe_2$, thin films

The $CuSe_2$ films were deposited by the spray pyrolysis method. The glass substrates was chemically cleaned. The spraying rate was 5 ml/min. 20 ml solution was sprayed to get films of thickness -~ 1 μm. The substrates were kept on hot substrate below the nozzle and aqueous solutions of copper chloride (0.05 M), and selenium dioxide (0.33 M). Temperature of the substrate was kept at 400°C and the spray rate, spray time was 5 ml / min., 8 min. respectively. In order to get films of higher thickness repeated deposition was carried out.The total area of the film deposited was 7. 5 × 2.5 cm it was divided into small cells of area $1cm^2$. The best cell was taken for characterization as a representative of the sprayed samples. The thicknesses of the films were measured by the weight difference techniques. The FTIR spectra were obtained for the $CuSe_2$, samples in the range of wave numbers from 4000 cm^{-1} to 400 cm^{-1}. The FTIR spectrophotometer used was α–Bruker, Nicolet MAGNA-IR760 combined with Nic-Plan IR Microscope. The optical absorption technique was utilized to estimate the absorption coefficient, energy band gap and the type of optical transitions. The optical densities were recorded for various incident wavelengths. A UV–Vis spectrophotometer (SHIMADZU-1700) was used for this purpose. The scanning wavelength range was from 300 nm to 1300 nm.

3. Results and Discussion

3.1 The FTIR studies

FTIR spectroscopy has been used to get the information about the possible structural units of the residues in the films. The FTIR measurements were conducted on the samples in the 4000 cm^{-1} to 500 cm^{-1} range. The peaks in the 3860 cm^{-1} to 3600 cm^{-1} range (i.e. at 3859 cm^{-1}, 3740 cm^{-1} and 3611 cm^{-1}) belong to OH^- stretching vibrations. The spectra showed different behaviour depending on the solution composition. The spectrum of Cu-rich film showed absorption bands indicating the reduced content of the phases having the vibrations in the mid-IR region. The vibrations at 2386 cm^{-1} and 2308 cm^{-1} are due to room atmosphere CO_2, which is not related to the sample material. The vibration near 1525 cm^{-1} belongs to NH_2.

The vibrations at 1070, 1050 and 670 cm^{-1} could be coupled with the sulfate (SO_4) group. The spectrum of Cu-rich film shows absorption bands and exhibit the vibrations at 3435 and 2170 cm^{-1} and the absorption at 1650 is so distained. The absorption peaks appear at 1125, 1290, 1730 and close to 2900cm^{-1}. The origin of the vibrations at 1125 and 1290 cm^{-1} is not declared as many functional groups could be responsible for the vibrations in this spectral region [7]. The vibrations close to 1730 cm^{-1} are characteristic for the carbonyl (C=O) group. The carbonyl group could appear as an oxidation product.

3.2 The optical absorption studies

The technique was employed to estimate the characteristic optical constants of a material in thin film form. Many materials like amorphous semiconductors, inhomogeneous metal-dielectric mixtures, etc can be prepared in the form of thin films. The optical techniques are fast in response, non-destructive and can easily be applied in situ in any transparent – ambient system and therefore are widely used for characterization of a variety of thin films [8]. The optical absorption spectra of the $CuSe_2$, thin films, corrected for glass - substrate absorption, were therefore obtained in the range of wavelengths from 300 nm to 1300 nm. The spectra were analyzed to evaluate the absorption coefficient (α), optical gap (Eg) and nature of the transition. Variation of α with wavelength λ, clearly indicated two regions; one for higher wavelengths with practically negligible absorption and other for lower wavelengths that correspond to the maximum absorption. It is found that the absorption coefficient of the order of 10^4 - 10^5 cm-1. The absorption coefficient (α) and the photon energy (hν) are related as [8]:

$$\alpha = \left(\frac{A}{h\nu}\right)(h\nu - E_g)^m$$

where, A is a constant and m assumes values 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. For direct transitions, the absorption coefficient (α) and the photon energy (hν) are related as [8]:

$$\alpha h\nu = A(h\nu - Eg)^{1/2}$$

The absorption data were analyzed for the near edge optical absorption of the semiconductor. The film composition dependence of the absorption coefficient was determined for the samples in the Vis-near infrared region. The additional absorbance in the film is believed to be due to the presence of secondary phase at the grain boundaries [9,10]. The optical gaps were then determined from the $(\alpha h\nu)^2$ vs. hν variation. The optical gap of $CuSe_2$ is found to be 2.10 eV. The transition indices (m) were then calculated for the sample.

4.Conclusions

1. A simple automated chemical spray pyrolysis system has been designed and developed. $CuSe_2$ thin films deposited by this technique.
2. The optical band gap for $CuSe_2$ is calculated and it was 2.10 eV.
3. The optical absorption of this material is found to be high and therefore its use as an optronic material.

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