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Editors

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CONTENT

STUDIES OF COPPER SULPHIDE THIN FILMS DEPOSITED BY CBD TECHNIQUE

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Abstract:

Copper Sulphide (CuS) thin films deposited on glass substrates by the Chemical Bath Deposition technique. Copper Sulphide for copper and Thiourea for sulfur were used as sources for Copper and Sulphur ions respectively. Effect of bath temperature concerning the assets of copper sulphide films was studied. Optical characterization was done by using a UV- VIS spectrophotometer in the wavelength range of 200 nm to 1100 nm. Transmittance, absorbance and band gap were calculated. Band gap energy range was found in between 2.25 eV to 2.34 eV and these consequences that the films can appropriately be castoff in the formation of solar cells. XRD studies long-established that the thin films had hexagonal structure and confirmed the excellence of crystallinity of the films by acquisitive the bath temperature. Surface roughness, thickness of the films and grain size were also improved with increasing of bath temperature from 50 and 55 °C. However, the samples deposited at 55 °C showed comparable and uniform structure giving to SEM and EDAX pictures. Electrical transport readings exhibited that the films are semiconducting in nature. Highest room temperature electrical conductivity of 6.37×10^{-3} to 8.34×10^{-3} $(\Omega\text{-cm})^{-1}$ was observed for the films. Thermo power extents indicated similar manner of variations corresponding to the electrical conductivity and that the samples show n-type conduction. The bath temperature was one of the key deposition parameters that control the possessions of semiconductor thin films.

Keywords: CBD technique, XRD studies, SEM and EDAX, semiconductor thin films.

Introduction:

Thin films of copper chalcogenides have usual much consideration due to their extensive range of application in semiconducting devices such as in photovoltaic, optoelectronic devices, radiation detectors, and solar cell convertors. Copper Sulfide chalcogenides have been of much attention to scientists because they achieve a number of the requirements for numerous modern

electronic and optoelectronic devices such as LED's, photodiodes, etc. Copper Sulfide is one of the direct band gap semiconductors with a varied gap which make them interesting for photovoltaic performance [1]. The Copper sulphide is a base material for the construction of innovative quaternary compounds and have also been of excessive interest in research because after doping they offer good window material assets. CuS thin films are widely used as an absorber considerable in opto-electronics, solar cells, photothermal conversion, electroconductive electrodes, microwave shielding coatings and solar control coatings etc. [2-6]. Chemical vapour deposition, chemical bath deposition, spray pyrolysis, sputtering, electrodeposition and vacuum evaporation are broadly used methods for deposition of thin films. Chemical bath deposition technique is comfortable, low-cost and suitable method for large area preparation of thin films. Other beautiful feature of the CBD method is that, ternary and quaternary compounds can be easily formed without the use of any sophisticated instrumentation and process control [7]. Numerous studies have been designated on the CuS binary system in powder, bulk, and as thin films with different compositions and properties. Differences in the properties originated mainly by factors associated to phases equilibria, because of a strong tendency of Cu and S to form several metastable and nonstoichiometric phases. Detecting physical properties we found that our material has excellent photocatalytic properties. In this paper, the deposition was carried out under changed bath temperatures in order to inspect the structural, morphological and optical characteristics of the films. The possible applications of the film were showing from their properties.

Experimental detail

For the deposition of samples all the chemicals of AR grade were used and the solutions were prepared in double distilled water. The copper sulphide thin films were prepared by chemical bath deposition method using aqueous solutions of copper sulfate ($CuSO_4$) and Thiourea (H_2NCSNH_2) acted as a source of Cu^{2+} and S^{2-} ions, respectively. The experiment was carried out for temperature 50 ^{0}C and 55 ^{0}C. Before deposition the glass substrates were washed with soap and a soft stuff and then washed with distilled water; after that placed in a chromic acid solution for 24 h. Then, the substrates were cleaned with deionized water several times and chemically attacked in a water-nitric acid solution for 3 hours at slowly boiling. The glass slides were immersed vertically in an aqueous solution containing copper sulfate(0.5M, 10mL), thiourea (0.5 M,10mL), triethanolamine (3.0 mL), sodium hydroxide (5.0mL) and ammonia 10 M). Distilled water was used for the preparation of solution. The pH of resultant solution was adjusted to 10. The cleaned glass substrate was immersed vertically into beaker which placed inside a temperature bath. Film deposition time was kept 45 min. After the completion of deposition, the as deposited samples splashed with double distilled water and kept for characterization and analysis [8].

Characterization of the samples

Weight difference method was used to measure the thickness of the as deposited film. Optical absorption measurements were carried out using UV-Vis spectrophotometer in the wavelengths range from 200 - 1100 nm. Structure of the film was studied by an X-ray diffraction technique using Regaku Miniflex XRD machine. Range of 2θ values was from 20° to 80° and radiations used were CuKα with wavelength1.5406 Å. Chemical composition of the films was carried out using an energy dispersive spectrometer (EDAX), Quanta 200ESEM. Scanning electron microscopy (SEM) indexation was intended for the as deposited films. Electrical conductivities of the films were tested by a two point probe method in the temperature range from 300 - 500 K. Thermovoltages were also noted on these films in the temperature range of 300 to 500 K. Ag-paste was used as the contact material for TEP characterization.

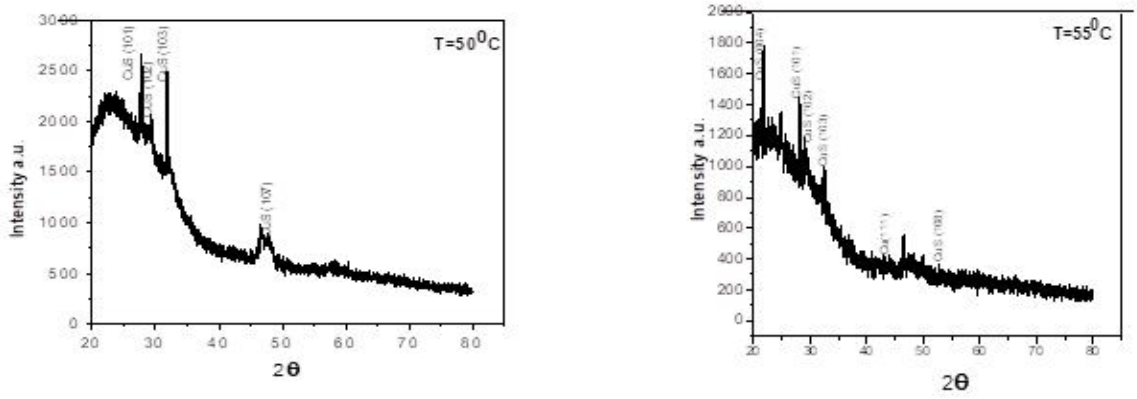
Results and Discussion:

The as-deposited thin films were smooth, transparent, absolutely adherent to the substrate, free of pinholes and reproducible. Typical XRD images of the CuS thin films prepared at 50°C and 55°C by the chemical bath deposition technique are illustrated in Figure 1.The chemical bath deposited CuS thin films are found to be polycrystalline in nature. The XRD shapes of the samples indicate presence of six peaks with different widths and intensities. These peaks are correspond to orientation along (004), (101), (102), (103), (111) and (108) planes of hexagonal phase of CuS [9, 10]. These peaks are well match with the standard JCPDS (79-2321) data. As per the bath temperature increases from 50 ^{0}C to 55 °C all the diffraction peaks become narrower and intensities of peaks increase signifying an enhancement of crystallinity. It means that the grain size increases with increase in the bath temperature. This plane seems dominant at this stage of experiment. It can be seen that the film crystallinity, grain size is mainly affected by bath temperature. From the XRD patterns, the peak (101) is considered as major peak with higher intensity. In our observed patterns of XRD the (102), (111), (107) and (105) planes are weak peaks and have lower intensity values. The crystallite sizes were calculated using Scherres relation. It is seen that crystallite size were in the nano range of 20.8 nm & 24.5 nm.

Figure 2 shows the chemical composition of the films was resolute by an energy dispersive spectroscopy (EDAX). The contents of Cu and S as taken in the deposition solution and that observed in the samples. It has been seen that CuS sample is Cu rich. It appears that S content is less than that of the expected (50 %), although the solution was taken to be in stoichiometric proportion.

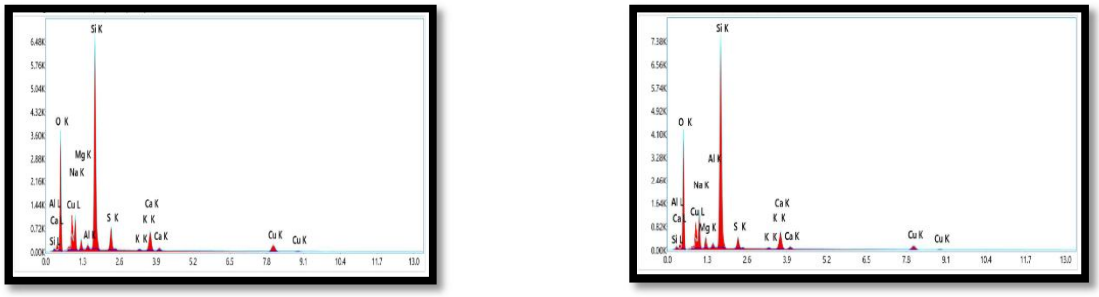
The absorbent nature of capacity of films can be detected from the SEM image of Figure 3 which indicates that nanodisks are arbitrarily concerned with in the space [10]. The influence of the temperature on the electrical properties of the CuS samples was estimated by two probe technique with Ag-dot contacts in a square sample of the 1 cm^2 with Van der Pauw configuration.

The samples exhibited n-type conductivity. The resistivity, the holes concentration, the mobility is calculated. The result of conductivity is correlated with measured thickness of samples (285nM and 335nM).



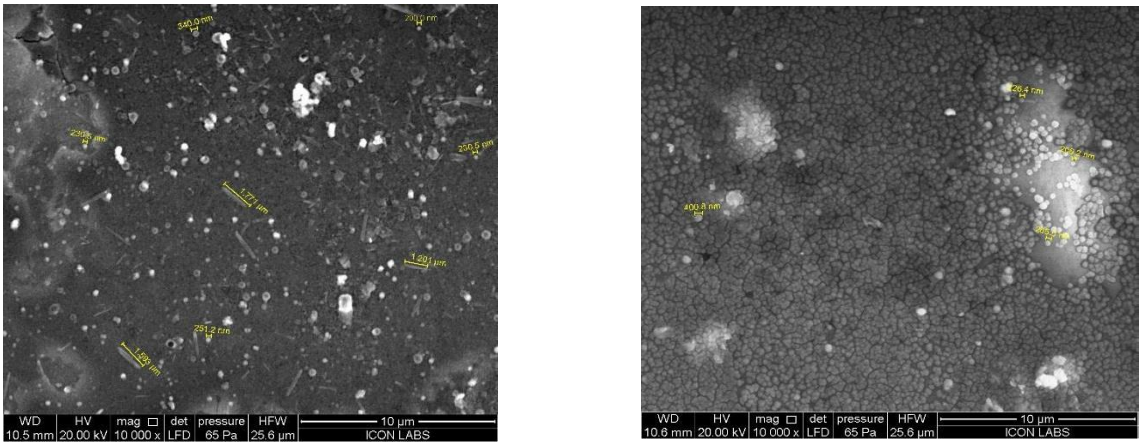
a **b**

Figure 1: X-ray diffraction patterns of CuS deposited at (a) temp. = 50 ^{0}C and (b) temp. = 55 ^{0}C



a **b**

Figure 2: EDAX of CuS thin film at (a) 50 ^{0}C and (b) 55 ^{0}C



a **b**

Figure 3: SEM images of a CuS thin films at (a) 50 ^{0}C and (b) 55 ^{0}C

CuS thin films deposited on glass substrate were characterized by the spectrophotometric technique for optical absorption in the 200 - 1100 nm wavelength range. The absorption data were examined for near edge optical absorption of semiconductor. For allowed direct transitions, n=1/2.The optical gaps were then determined frome the $(\alpha h\nu)^2$ vs $h\nu$ variation and an energy bandgap with temperature as shown in figure4. It is seen that E_g increased with increase in temperature [10]. The optical gap of pure CuS is found to be 2.25 eV and 2.34 eV.

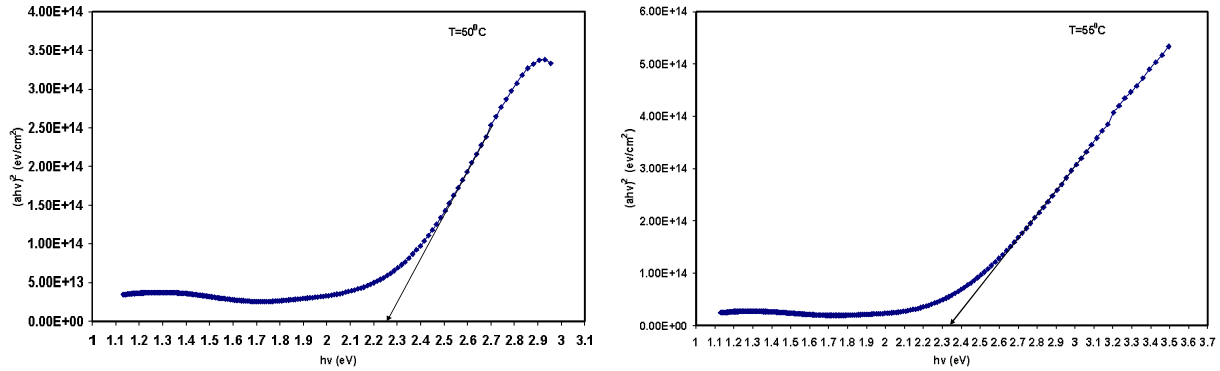


Figure 4: Bandgap of CuS samples

The electrical conductivities of the as deposited CuS thin films were measured using two-probe method in the range of temperature from 300 – 500 K. Fig.5 shows variation of the electrical resistivity with film temperature. The films are semiconducting and nonlinear nature and show presence of many defects in the films.The increase in electrical conductivity can be attributed to increase in the particle size. The type of conductivity revealed by the chemically deposited CuS thin film is determined from TEP measurements. It is found that CuS exhibits n-type conduction.

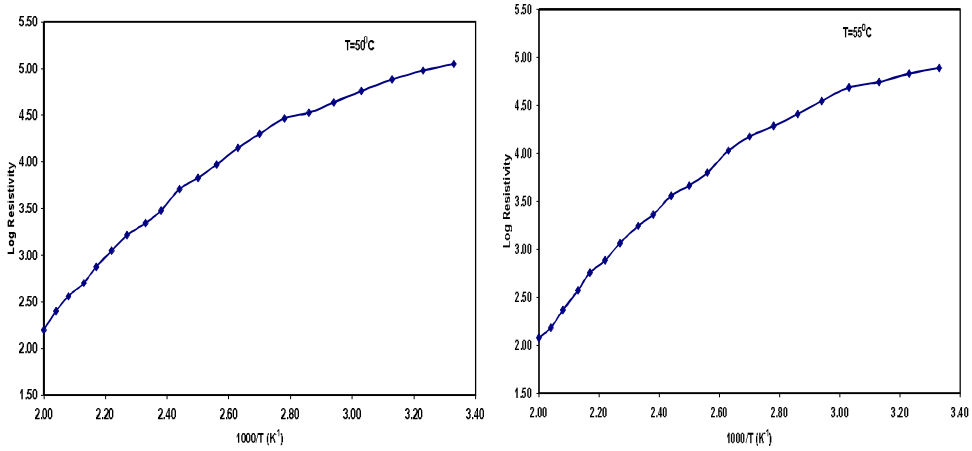


Figure 5: Variation of the electrical resistivity with film temperature

Conclusions:

Thin films of Copper Sulphide have been grown on glass substrate using chemical bath method at changing temperature and characterized to study the structural property using EDAX, SEM, XRD and Spectrophotometer to determine its optical properties. It is observed that the film absorbance is high in UV region and low in VIS NIR region while the transmittance is low in UV region and high in VIS – NIR regions. The energy band gap of the film obtained is between 2.25eV and 2.34eV. These results propose that the films can appropriately be used in the construction of solar cells.

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About Editors

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Mr. Somnath Shivram Sanap has completed M.sc Mathematics from K.T.H.M. College Nasik. He also qualified SET exam in Mathematics. He has an experience of more than 11 years of teaching to under graduate level. He taught various subjects of Engineering and B. Sc. at UG & PG level. He has published two book chapters in different books and presented two research papers at national and international conference. He has contributed in various college level committees and student centric activities.

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