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RESEARCH ARTICLE

COPPER SULPHIDE THIN FILM BY A LIQUID PHASE CHEMICAL BATH GROWTH PROCESS

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Abstract

Deposition of copper sulphide (CuS) thin films was carried out using liquid phase chemical bath deposition process at the optimized growth parameters as: 70 ^{0}C deposition temperature, 45 minutes deposition time, pH equal to 10 ± 0.1. The as grown deposits exhibited excellent uniformity and physical adherence with the substrate surface and are smooth and diffusely reflecting with dark chocolate colour during deposition. The layer is of the order of 270 nm thick. The EDS analysis technique gave film composition to be nearly stoichiometric (Cu = 48.50 %, S = 51.50 %). The X-ray diffraction analysis showed CuS to be hexagonal with a good match of d – values and intensities of reflections. The crystallite size is in the nano range 18.8 nm. The as-deposited CuS exhibited a high coefficient of absorption with a direct optical band gap of 2.15 eV. Compared to other chalcogenides, CuS films exhibit low resistance. The electrical conductivity decreased with increase in temperature up to 473 K; showing totally unusual behaviour from that of the semiconducting property. The two point thermo probe measurements showed n – type conduction and highest conductivity was 2.19 × 10^{-2} $(\Omega.cm)^{-1}$.

Keywords: Optimized growth, physical adherence, hexagonal, crystallite size and Semiconducting property

Introduction

The CuS be real in a wide range of its stoichiometric composition and different crystallographic forms allowing for engineering of the materials properties thereby croft scientific and technological potential in solar absorber and control applications. It is an excellent precursor material for the fabrication of Cu (In/Ga) Se based solar cells and that it can be synthesized using a chemical solution deposition or chemical bath deposition, which provides stoichiometric precipitate precursor, in addition to good quality yield of CuS thin films. The technique provides in-situ research of the films and is ideally suited for the production of large area thin films. The film homogeneity inclines to be very good because growth is often under kinetic control via surface reactions. The large area capability, ease of scaling up with complete control of materials handling in solid or liquid phase, and the applications in the area of solar

energy conversion have encouraged improved interest in chemically deposited thin films. The deposition background of the chemical bath deposition process and the factors affecting growth mechanism and crystallite size, it is a truthful optimism to deposit CuS thin films of desired structure, morphology, composition, optical and electrical properties and thermal stability in the situation of their use as an optoelectronic material. In this work, the chemical bath deposition technique has been used to prepare CuS thin films and investigating the structure, optical, and electrical properties (Suryawanshi *et al.*, 2021; Ahmed *et al.*, 2020; Mohammed *et al.*, 2020; Osuwa and Mgbaja 2013).

Experimental Techniques

Preparation of CuS thin films

In the chemical bath growth process, it is important to control the preparation conditions such as the concentration of solutions, pH of the solutions time for deposition and the temperature. Good quality thin films of CuS were prepared by using aqueous solutions of copper sulfate ($CuSO_4$) and Thiourea (H_2NCSNH_2) as a source of Cu and S individually. The experiment was carried out for temperature 70 ^{0}C. Microscope glass substrates have been passed through the cleaning stage before deposition in the dilute sulfuric acid and it was then cleaned with acetone and made ready for deposition by washing through pure water. Ready glass slides were deep vertically in an aqueous solution having copper sulfate, thiourea (0.5molarity and 10ml of each), triethanolamine, sodium hydroxide and ammonia were used as a complexing agent. All the solutions were prepared in double distilled water. The pH of the solution was maintained to 10. After (45mini.) the completion of deposition, films were eroded with distilled water (. Saritha *et al.*, 2013; Tuba Çayır Taşdemirci 2019; Suryawanshi *et al.*, 2023)

Characterization tools and techniques

Thickness of the as-deposited CuS layer was measured by an optical interferometry technique. The film composition was determined by an EDS technique (EDS spectrometer). The X-ray diffraction technique was used to determine structure of the CuS thin layer. with CuKα line (λ = 1.5406 A^0), 2θ = 20^0-80^0. The surface morphology was seen through a scanning electron microscope. The optical constants such as absorption coefficient, optical gap and the type of transitions for the sample were then determined from the measurement of optical absorbance spectra. The dc electrical conductivity and thermoelectric power measurements in the 300-550K temperature range were recorded.

Results and Discussion

Copper sulphide material hold promise for applications in the areas of visible and infrared light emitting diodes, infrared detectors, optical parametric oscillators, up converters and in solar energy conversion including recent higher order (CIGSSe) type devices. Assembly of these devices demands multi-step deposition technologies that require a low cost economic and industrially exploited deposition method. CuS thin films were therefore synthesized in view for the clarification of structure, composition, optical, and electrical properties and thermal stability in the context of its use as an optoelectronic grade material. It has been seen that as-grown deposits are smooth, uniform physically adherent and diffusely reflecting with dark chocolate during deposition. The layer thickness is around 270 nm. The EDS analysis showed that, Cu = 48.50 %, S = 51.50 %), fig. 1. (Deshmukh *et al.*, 2012; Parlak and Ercelebi 1998; Reddy 2003; Nithyaprakash *et al.*, 2010).

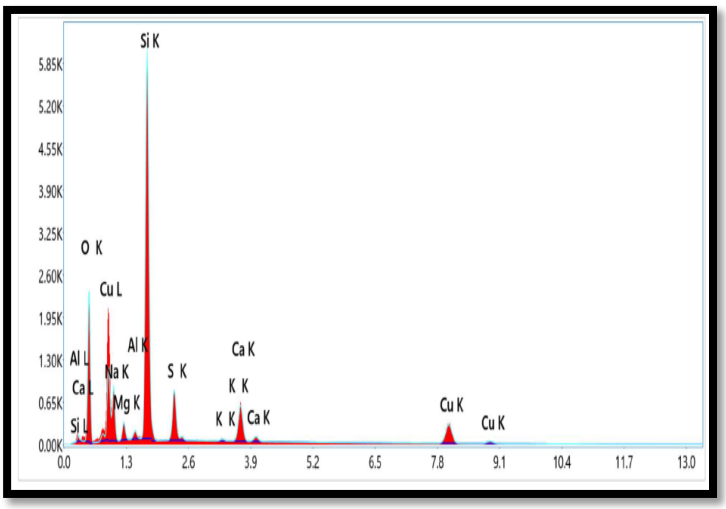

Fig. 1: EDS spectrum of CuS thin film deposited at 70^0

The XRD studies fig. 2 in the 20^0 – 80^0 2Θ range with CuKα = 1.5406 A^0 showed the low-intensity and inclusive diffraction peaks express that the films contain of coarsely well grains and are nanocrystalline in nature. The orientations, namely (102), (107) and (200) which indicate a covellite CuS phase with hexagonal structure.

Crystallite dimensions value has been found as 28.5 nm. Results are effective in the development of the crystal structure of CuS thin films. (Zhong et al., 2013; Sabah et al., 2016).

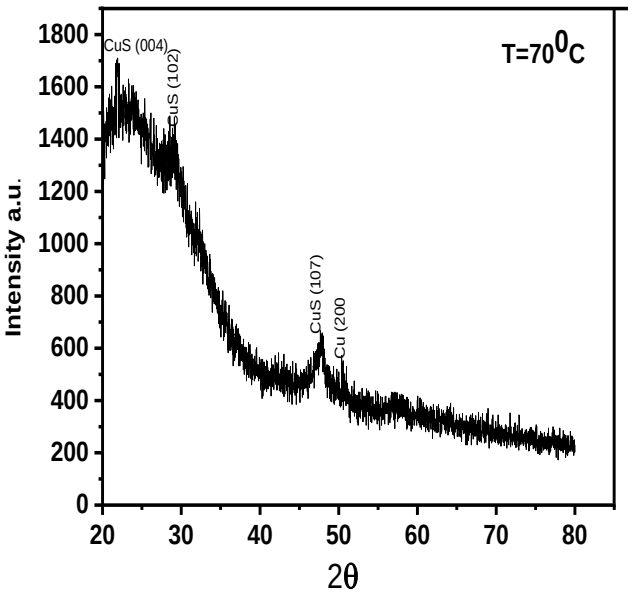

Fig.2: The x-ray diffraction of CuS thin films at 70°C.

Morphology of the prepared thin film was studied using SEM which shows the surfaces in high magnification and high resolution. The image of CuS thin films prepared is shown in Figure 3. It observed that the prepared CuS thin films have cauliflower-like forms with an irregular particle sizes and have some cracks and voids resulting from crystalline defects. (Nithyaprakash *et al.*,2010; Zhong *et al.,* 2013). The average grain size value of sample is found to be 581nm.

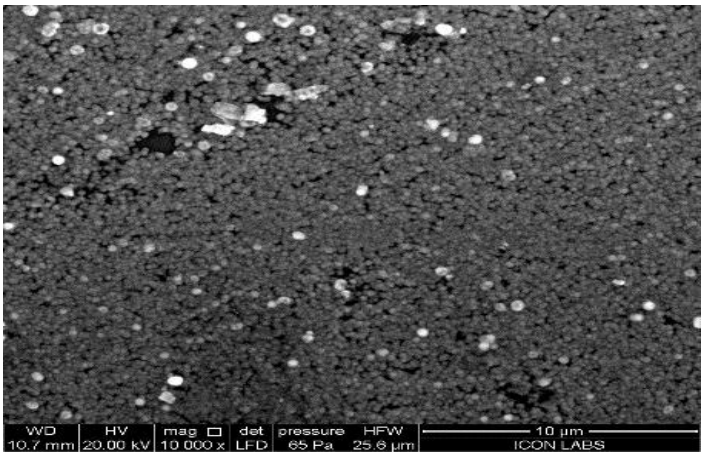

Fig.3: SEM image of CuS thin films at 70 ^{0}C

The absorption coefficient as a function of the wavelength of the CuS thin films. The acquired results showed high values of the absorption coefficient in the visible spectrum and ultraviolet, representing a high prospect of direct electronic transitions. The energy gap value of direct electronic transitions was calculated by plotting a graphical relationship of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$). The energy gap values for the CuS films was found to be in the range of 2.15 eV. This values are very adjacent to those used for solar cell applications. 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. The highest electrical conductivity value was found to be 2.19×10^{-2} $(\Omega.cm)^{-1}$ for the film deposited at 70 °C. 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 (Bakr 1986).

Conclusions

Nanostructured CuS thin films were prepared by the chemical bath deposition method. From XRD analysis it was concluded that film have hexagonal structure. The films are n-type in nature. The substrate temperature 70 °C is notable by having the best structural, electrical and optical properties. The properties of the prepared films suggest that they can be a good candidate for absorbent layer in solar cells.

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