Research Article

Ultrasonic Spray Pyrolysis Deposited Copper Sulphide Thin Films for Solar Cell Applications

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Polycrystalline copper sulphide (Cu\textsubscript{x}S) thin films were grown by ultrasonic spray pyrolysis method using aqueous solutions of copper chloride and thiourea without any complexing agent at various substrate temperatures of 240, 280, and 320°C. The films were characterized for their structural, optical, and electrical properties by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX), atomic force microscopy (AFM), contact angle (CA), optical absorption, and current-voltage (I-V) measurements. The XRD analysis showed that the films had single or mixed phase polycrystalline nature with a hexagonal covellite and cubic digenite structure. The crystalline phase of the films changed depending on the substrate temperature. The optical band gaps (E\textsubscript{g}) of thin films were 2.07\,eV (CuS), 2.50\,eV (Cu\textsubscript{1.765}S), and 2.28\,eV (Cu\textsubscript{1.765}S–Cu\textsubscript{2}S). AFM results indicated that the films had spherical nanosized particles well adhered to the substrate. Contact angle measurements showed that the thin films had hydrophobic nature. Hall effect measurements of all the deposited Cu\textsubscript{x}S thin films demonstrated them to be of p-type conductivity, and the current-voltage (I-V) dark curves exhibited linear variation.

1. Introduction

Copper sulphide (Cu\textsubscript{x}S) has attracted a great deal of scientific attention due to the tunable semiconductive properties and approximate metallic behaviors depending on stoichiometry of the mineral phase [1]. In a variety of techniques, it represents a promising p-type semiconductor used in a variety of technologies such as nanoscale electronic devices, cathode material of lithium ion batteries, chemical sensors, and especially photovoltaic cells because of its unique optical and electronic characteristics [2–7]. There are five stable phases of Cu\textsubscript{x}S at room temperature which vary according to values of x (1 ≤ x ≤ 2): chalcocite (Cu\textsubscript{2}S), djurleite (Cu\textsubscript{1.95}S), digenite (Cu\textsubscript{1.8}S), anilite (Cu\textsubscript{1.75}S), and covellite (CuS) [8, 9]. Because of these different phases, the energy band gap of Cu\textsubscript{x}S thin films varies between 1.26 and 2.54\,eV [10–15].

Many studies have been carried out on Cu\textsubscript{x}S films prepared by various techniques such as chemical vapor deposition (CVD) [16], RF sputtering [17], vacuum thermal evaporation [18], spray pyrolysis [19–21], and chemical bath deposition (CBD) [22]. Among these methods, ultrasonic spray pyrolysis (USP) is a suitable method for preparation of Cu\textsubscript{x}S thin films [23–25]. The ultrasonic spray pyrolysis technique is a simple coating technology in which an aqueous solution containing compounds in the form of soluble salts of each element is sprayed onto heated substrates. In addition, this process also enables growth of easily nanostructured and high quality thin films and control of film thickness and stoichiometry. In this technique, inexpensive equipment is used, and high quality chemicals and substrates are not necessary compared with the other techniques. The USP is promising due to low cost, easy processability, and the possibility of fabricating large area films with satisfactory structural quality [26]. In USP technique, some parameters such as substrate temperature, molar ratio, type of salt, and pH of the solution change the physical properties of the thin films [27]. Crystalline structure, grain size, optical bad gap, semiconductor type, the ratio of elemental composition, and surface morphology of the deposited thin films can be configured by controlling these USP parameters.

In the present investigation, an attempt was made to deposit polycrystalline Cu\textsubscript{x}S thin film of copper sulphide...
on glass substrates by ultrasonic spray pyrolysis method. Structural, morphological, electrical, and optical properties of copper sulphide thin films were investigated as a function of substrate temperature. Contact angle analysis of the copper sulphide film surfaces was performed depending on the substrate temperature for the first time. We try to explain crystalline phase transitions when the films are deposited at higher temperatures. To our knowledge, such a detailed study on the effect of substrate temperature on the properties of copper sulphide thin films is still lacking.

2. Experimental Details

2.1. Deposition of Cu,S Thin Films. In the USP technique, a precursor aerosol is sprayed towards the substrate. The constituents in the precursor droplets interact to form a new chemical compound on the substrate surface. The physical properties of the deposited film vary depending on the composition of solution, spraying rate, substrate temperature, ambient atmosphere, carrier gas, droplet size, and the distance between spray nozzle and substrate. The Cu,S films were deposited using an ultrasonic spray pyrolysis (USP) technique at different substrate temperatures. Details of the USP technique were described elsewhere [28]. Solution was prepared using a mixture of aqueous solutions of 0.01 M CuCl₂-2H₂O and 0.05 M thiourea, CS(NH₂)₂. Copper chloride (purity 99.9%) and thiourea (purity 99.0%) were purchased from Sigma-Aldrich. The films were deposited through ultrasonic nozzle onto microscope glass substrates (1 × 2 cm²) using air as the carrier gas with pressure of 1 atm. The ultrasonic oscillator frequency was 100 kHz. Deposition time was 20 min and total solution sprayed onto substrates was 100 cc. The solution flow rate was kept at 5 cc/min by a flowmeter. The distance from nozzle to substrate was kept constant at 3 cm. Thesolutionflowratewaskeptat5cc/minbyaflowmeter. Ultrasonicoscillatorfrequencywas100kHz. Deposition time was 20 min and total solution sprayed onto substrates was 100 cc. The solution flow rate was kept at 5 cc/min by a flowmeter. The distance from nozzle to substrate was kept constant at 36 cm. The films were formed at three different substrate temperatures, 240, 280, and 320°C. Substrate temperature was controlled by an iron-constant thermocouple within ±5°C. In the work, the thin films deposited at 240, 280, and 320°C substrate temperatures are called TF1, TF2, and TF3, respectively.

2.2. Thin Film Characterization. Characterization of the deposited films was performed using a mixture of aqueous solutions of 0.01 M CuCl₂-2H₂O and 0.05 M thiourea, CS(NH₂)₂. Copper chloride (purity 99.9%) and thiourea (purity 99.0%) were purchased from Sigma-Aldrich. The films were deposited through ultrasonic nozzle onto microscope glass substrates (1 × 2 cm²) using air as the carrier gas with pressure of 1 atm. The ultrasonic oscillator frequency was 100 kHz. Deposition time was 20 min and total solution sprayed onto substrates was 100 cc. The solution flow rate was kept at 5 cc/min by a flowmeter. The distance from nozzle to substrate was kept constant at 36 cm. The films were formed at three different substrate temperatures, 240, 280, and 320°C. Substrate temperature was controlled by an iron-constant thermocouple within ±5°C. In the work, the thin films deposited at 240, 280, and 320°C substrate temperatures are called TF1, TF2, and TF3, respectively.

3. Results and Discussion

3.1. Structural Properties. The X-ray diffraction patterns (XRD) were recorded for all the films in the range of diffraction angle 2θ between 20 and 70°. Figures 1–3 show XRD patterns of the Cu,S thin films deposited on glass substrates at three different temperature conditions. The X-ray diffraction pattern of these films revealed that these materials were polycrystalline phases: CuS, Cu, and Cu,S. The X-ray diffraction pattern of these films revealed that these materials were polycrystalline phases: CuS, Cu, and Cu,S. Well-defined (1 0 1), (1 0 2), (1 0 3), (1 1 0), and (1 1 6) peaks at 2θ = 27.74°, 29.48°, 31.76°, 48.24°, and 59.64° are observed in the XRD pattern due to hexagonal covellite phase of CuS (the lattice parameters are as follows: a = b = 3.792 Å, c = 16.344 Å) for the TF3 film. In Figure 1. The result is in agreement with the data given in the work by Zhu et al. [29] and in standard values (JCPDS 6-0464). Figure 2 shows the XRD for the TF2 film. The diffractions peaks at 2θ values of 28.16°, 32.26°, 46.46°, and 54.8° can
From the XRD patterns of the Cu$_x$S films, we conclude that the high substrate temperature leads to a phase transition from Cu$_{1.765}$S to Cu$_2$S.

The broadness of the full width at half maximum (FWHM) of the main diffraction peak indicates the formation of nanocrystals [22]. The average crystallite size of the Cu$_x$S films for the peak with highest intensity can be estimated by using Scherrer’s formula [30]:

$$D = \frac{0.9\lambda}{\beta \cos \theta},$$  \hspace{1cm} (1)

where $\lambda$ is the wavelength of Cu-K$_\alpha$ radiation (1.5406 Å), $\beta$ is the broadening of diffraction line measured at half maximum intensity (in radians), and $\theta$ is the diffraction angle.

The crystallite size was calculated by using the well-known Scherrer formula. The calculated crystallite size varies between 11.92 nm and 9.6 nm for TF1–TF3 materials (Table 1). The results indicate that crystallite size decreases as deposition temperature of the films increases.

3.2. Scanning Electron Microscopy and Energy Dispersive X-Rays Analysis. Figure 4 shows the surface characteristics of the Cu$_x$S thin films. These films are uniform, dense, and smooth and cover the glass substrate very well. A clear change in the surface formations of the thin films is seen when substrate temperature changes. In the first film, TF1, the surface shows large and small particles in different shapes, and there are no empty spaces between them (Figure 4(a)). The SEM image of TF2 (Figure 4(b)) demonstrates homogeneous distribution of the observed grains with dimensions on the order of 400 nm. There exist a lot of elongated particles with the lengths varying from 900 nm to 100 nm, as well as ellipsoid and circular pieces, on the surface of TF3 (Figure 4(c)).

Energy dispersive analysis of X-rays (EDAX) provides quantitative information about the composition of the thin films. The EDAX results about atomic percentages of Cu and S elements in TF1, TF2, and TF3 thin films are in close agreement with the X-ray diffraction (XRD) results (Table 2).

3.3. Atomic Force Microscopy Studies. The control of the surface properties is important in developing for the physical characteristics of the films. Atomic force microscopy (AFM) is used to determine nanoscale surface morphology of the deposited films. These AFM observations allow for controlling surface properties by changing film deposition parameters. Figure 5 shows three-dimensional (3D) AFM scans of the crystallized Cu$_x$S thin films grown by USP on glass substrates at 240, 280, and 320°C. The images show that the surface topography is typical, and the morphology of the film indicates roughness and shaped crystallites [7, 31]. The surface rms roughness values of the TF1, TF2, and TF3 thin films are 54.0, 47.2, and 24.3 nm, respectively. The average rms roughness of the films decreases remarkably as the film production temperature increases from 240°C to 320°C. The increase in substrate temperature also brings about an increase in Cu/S ratio of the films. The AFM images of the Cu$_x$S thin films represent the fact that each of the films...
Table 1: Comparison of observed XRD data of thin films with the JCPDS cards. The film thickness, lattice type, crystallite size calculated by Scherrer formula, and contact angle are also summarized.

| Thin film | Film thickness (nm) | Observed values 2θ (°) | d (Å) | Standard values 2θ (°) | d (Å) | hkl | Phase | Lattice | Crystallite size D (nm) | Contact angle (°) |
|-----------|---------------------|------------------------|-------|------------------------|-------|-----|-------|---------|------------------------|------------------|
| TF1       | 160                 | 27.74                  | 3.22  | 27.68                  | 3.22  | (1 0 1) | CuS   | Hexagonal | 11.92                  | 96.60            |
|           |                     | 29.48                  | 3.03  | 29.28                  | 3.05  | (1 0 2) | CuS   | Hexagonal |                        |                  |
|           |                     | 31.76                  | 2.80  | 31.79                  | 2.81  | (1 0 3) | CuS   | Hexagonal |                        |                  |
|           |                     | 48.24                  | 1.89  | 47.94                  | 1.90  | (1 1 0) | CuS   | Hexagonal |                        |                  |
|           |                     | 59.64                  | 1.55  | 59.35                  | 1.56  | (1 1 6) | CuS   | Hexagonal |                        |                  |
| TF2       | 380                 | 28.16                  | 3.18  | 27.95                  | 3.19  | (6 6 2) | Cu\textsubscript{1.765}S | Cubic | 10.80                  | 107.83           |
|           |                     | 32.26                  | 2.76  | 32.27                  | 2.77  | (10 0 0) | Cu\textsubscript{1.765}S | Cubic |                        |                  |
|           |                     | 46.46                  | 1.95  | 46.21                  | 1.96  | (14 2 0) | Cu\textsubscript{1.765}S | Cubic |                        |                  |
|           |                     | 54.80                  | 1.67  | 54.79                  | 1.67  | (15 7 1) | Cu\textsubscript{1.765}S | Cubic |                        |                  |
| TF3       | 172                 | 27.92                  | 3.18  | 27.95                  | 3.19  | (6 6 2) | Cu\textsubscript{1.765}S | Cubic | 9.60                   | 96.97            |
|           |                     | 32.44                  | 2.76  | 32.27                  | 2.77  | (10 0 0) | Cu\textsubscript{1.765}S | Cubic |                        |                  |
|           |                     | 46.62                  | 1.95  | 46.28                  | 1.96  | (2 2 0) | Cu\textsubscript{2}S  | Cubic |                        |                  |
|           |                     | 54.78                  | 1.67  | 54.79                  | 1.67  | (15 7 1) | Cu\textsubscript{1.765}S | Cubic |                        |                  |

Figure 4: SEM micrographs of (a) TF1, (b) TF2, and (c) TF3.

is continuous and homogeneous and has no discontinuities or cracked areas (Figure 5).

3.4. Contact Angle Measurements. The contact angle is a macroscopic parameter, which is a consequence of the intermolecular interactions between a liquid and a solid in contact. Contact angle measurements are used to obtain information about the degree of these interactions. Figure 6 shows the photo-images of water contact angle measurements on the Cu\textsubscript{x}S thin films and glass substrate. The water contact angle was equal to 25.76° for untreated glass substrate (Figure 6(a)). The water contact angle measurements on TF1, TF2, and TF3 Cu\textsubscript{x}S thin films were found to be 96.60°, 107.83°, and 96.97°, respectively, which show hydrophobic nature of the films (Figures 6(b)–6(d)). The surface porosity of TF1 and TF3 is seen to be similar from the SEM and AFM images (Figures...
Figure 5: AFM image of (a) TF1, (b) TF2, and (c) TF3.

Table 2: Comparison of EDAX and XRD data.

| Thin film | Element | C norm. (wt.%) | C error % | Cu/S ratio (EDAX) | Cu/S ratio (XRD) |
|-----------|---------|----------------|-----------|-------------------|------------------|
| TF1       | Cu      | 52.24          | 0.2       | 1.094             | 1.000            |
|           | S       | 47.76          | 0.2       |                   |                  |
| TF2       | Cu      | 63.89          | 0.6       | 1.769             | 1.765            |
|           | S       | 36.11          | 0.5       |                   |                  |
| TF3       | Cu      | 64.13          | 0.6       | 1.788             | 1.765 and 2.000  |
|           | S       | 35.87          | 0.4       |                   |                  |

4 and 5). The contact angles are almost equal to each other for TF1 and TF3 due to this similarity. The surface of TF2 thin film is composed entirely of small and regular grains, while the surface of both TF1 and TF3 has not uniform grain structure. From SEM and AFM observations (Figures 4 and 5), it is concluded that the value of the contact angle is directly correlated with the nanoscale structure of film surfaces. As a result, TF2 has a highest contact angle value of 107.83° due to its different surface topography.

3.5. Optical Properties. The optical transmittance spectra of Cu₅S films obtained for different deposition temperatures in the range of 200–1100 nm were shown in Figure 7. The transmittance values of the films except for TF1 increase dramatically between 400 and 700 nm wavelength range. The results show that different deposition temperatures are effective on the optical and structural parameters of the films. As seen in XRD pattern of Cu₅S films (Figures 1–3), changing the deposition temperature results in occurrence of different Cu₅S phases. It was found that TF1, TF2, and TF3 films had an average T value of ~33%, 65%, and 55% in the visible region, respectively. For TF2 and TF3 films, there is a significant increase in T% values depending on the deposition temperature. It is clear that the transmittance of the samples increases as the substrate temperature increases. The thicknesses of TF1, TF2, and TF3 are 160, 380, and 172 nm, respectively. Thus, the film with higher thickness shows an increase in transmittance.

The optical band gaps ($E_g$) for Cu₅S films were also studied and these values were determined using Tauc’s law [32, 33]:

$$a h v = A (h v - E_g)^n,$$

(2)
Where $\alpha$ is the absorption coefficient, $h\nu$ is photon energy, $E_g$ is energy band gap, $A$ is the edge parameter, and $m$ is a constant for a given transition (the value of $m$ is 1/2 for direct allowed transitions and 2 for indirect allowed transition).

Figure 8 shows plots of square of the product of the optical absorption coefficient ($\alpha$) and photon energy ($h\nu$) against photon energy. The values of the energy band gaps for the TF1, TF2, and TF3 films are 2.07, 2.50, and 2.28 eV, respectively. It was found that the energy band gaps of the films varied with not only deposition temperature but also Cu$_x$S phases. XRD pattern given in Figure 1 is evidence that TF1 thin film has CuS single phase, and the calculated energy band gap ($E_g$) using experimental data for TF1 thin film is in agreement with the $E_g$ value reported by Grozdanov and Najdovski [34] and by Zhu et al. [29]. The XRD data shows that TF2 has single phase of Cu$_{1.765}$S. There is no report of $E_g$ values for Cu$_{1.765}$S in the literature, but we have estimated that the $E_g$ value of Cu$_{1.765}$S is between Cu$_{1.8}$S (2.3 eV) [13] and Cu$_{1.75}$S (2.54 eV) [12]. The XRD pattern in Figure 3 demonstrates that TF3 thin film includes both Cu$_{1.765}$S and Cu$_2$S phases; that is, this film is a mixture of Cu$_{1.765}$S and Cu$_2$S phases. So, there is a small decrease in $E_g$ value compared with TF2 thin film. The reason of this decrease for TF3 thin film may be attributed to having Cu$_2$S phase component (1.5 eV) [15] in the mixed phase. Consequently, both optical and structural results found by evaluated experimental data for the films support each other.

3.6. Electrical Properties. Hall effect measurements were performed to characterize the electrical properties of the Cu$_x$S films and all the films showed a p-type semiconductor with hole concentration in the range of $(1.45-2.64)\times10^{21} \text{ cm}^{-3}$ and hole mobility $(1.96-11.8)\times10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}$. Carrier concentration, Hall mobility, Hall coefficient, and sheet resistance values were obtained by four-point probe technique using Hall effect measurement system in a magnetic field strength of 0.556 T and these values were listed in Table 3. As shown in Table 3, all the films present high sheet resistance of $(1.25-7.67)\times10^3 (\Omega \text{ cm})^{-1}$. It is observed that the carrier mobility values of the films increase as the film crystallite size increases (Tables 1
Table 3: Carrier concentration, Hall mobility, Hall coefficient, sheet resistance, and optical gap values of the Cu$_x$S thin films.

| Cu$_x$S sample | Carrier concentration ($\times 10^{21}$ cm$^{-3}$) | Hall mobility (cm$^2$/Vs) | Hall coefficient ($\times 10^{-4}$ cm$^3$/C) | Sheet resistance ($\times 10^3$ Ω) | Optical gap (eV) |
|----------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| TF1            | 2.64                            | 1.18 $\times 10^{-2}$ | 4.42             | 1.25             | 2.07            |
| TF2            | 1.45                            | 8.64 $\times 10^{-3}$ | 1.56             | 1.29             | 2.50            |
| TF3            | 2.41                            | 1.96 $\times 10^{-3}$ | 2.35             | 7.67             | 2.28            |

Figure 9: Current-voltage variations for copper sulphide thin films at room temperature.

and 3). It is in agreement with the study reported earlier about Cu$_x$S films [18]. The current-voltage (I-V) curves of the films are obtained in dark (Figure 9). The current increases linearly with the voltage, as seen in Figure 9. Such differences in the I-V curves of the films can be correlated with film thickness and/or with amount of defects.

4. Conclusions

Copper sulphide thin films were deposited onto glass substrate by spray pyrolysis technique at temperatures 240, 280, and 320 °C. It was found that crystalline phase, crystallite size, and surface uniformity of the films were very sensitive to the substrate temperature. The increase of substrate temperature caused crystallite size of the film to decrease by 11.92 nm to 9.60 nm. The film phase was CuS at 240 °C and Cu$_{1.765}$S at 280 °C. The copper sulphide thin film exhibited polycrystalline structure composed of Cu$_{1.765}$S and Cu$_2$S phases when substrate temperature reached 320 °C. AFM analysis showed that the surface rms roughness decreased from 54.0 nm to 24.3 nm with the increase of substrate temperature. Sheet resistance of the films increased depending on the increasing substrate temperature. From the optical studies, direct energy band gap values of the films were determined to vary between 2.07 and 2.50 eV. However, any information or data about dependency of optical band gap of the films on substrate temperature could not be found in the literature. In addition to this, optical band gap was found to be dependent on the film thickness and increased from 2.07 to 2.50 eV when film thickness was increased from 160 to 380 nm. The current-voltage variations for Cu$_x$S thin films were determined to be linear. These films had a p-type semiconductor behavior.

Cu$_x$S thin films produced in this study can be used in heterojunction solar cells due to their good crystalline structure and energy band gap value matching well solar radiation. Spray pyrolysis deposition represents a low cost technique, allowing the development of large area thin films for solar energy conversion devices.

Competing Interests

The authors declare that there is not any conflict of interests.

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