Research Article
Preparation and Characterization of Nanocrystalline CuS Thin Films for Dye-Sensitized Solar cells

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1. Introduction

Recent research on solar cells has been aimed at lowering the fabrication cost to decrease the price of the energy obtained. In this context, suitable materials should be easily preparable, inexpensive, and must show stable behavior over a long period of operation. The photo electrochemical (PEC) cells provide an economic chemical route for trapping solar energy. Beside the PEC cell, the semiconductor-electrolyte interface may be used for photocatalysis, and photoelectrochemical power generation [1]. Thus the PEC cells composed of dye-sensitized oxides have also been widely investigated. Several natural pigments [2] and synthesized dyes [3] have been identified to fabricate the solar cells. The dye-sensitized (DS) PEC cell based on nanocrystalline TiO 2 [4] and the DSSC with solid hole collectors are reported elsewhere [5]. Nanocrystalline metal sulphide such as copper sulphide (CuS), deposited as a thin film on the different substrates, is considered as a promising material for solar energy conversion system, due to their structural and electrical properties [6]. It is used in a variety of applications, namely, as gas sensor [7] and optoelectronic devices as reported by Nair et al. [6, 8]. Several techniques have been used to produce copper sulphide thin films such as spray pyrolysis [9, 10], successive ionic layer absorption and reaction techniques [11], photoelectrolysis, and photoelectrochemical power generation [1]. Among them the chemical bath deposition (CBD) method is attractive since the technique possesses a number of advantages over conventional thin film deposition methods. CBD technique is used for producing a thin film of copper sulphide, and the effect of time on deposition at various concentrations is also studied [17]. The effects of film thickness on structural, optical, and electrical properties of the as-deposited nanocrystalline copper sulphide thin films [18] and fabrication CuS films at high temperature and its effect on optical property of the film [19] have also been reported. This technique is the most cost saving and convenient to produce various chalcogenide thin films such as In 2 S 3 [20], CdSe [21], SnS [22], and FeS [23]. It makes use of the fact that film can be deposited on
a suitable substrate by dipping them in a suitable solution bath containing metal salts without applying any external field. Even though there are physical techniques which are more suitable for the growth of uniform and high-quality thin films, they are expensive and require more efforts, whereas chemical methods are economical and simple.

In the present report, an attempt is made to develop a nanocrystalline copper sulphide thin film on ITO-coated glass substrate by CBD technique. For the first time CV organic dye (a photosensitizer) is adsorbed over CuS thin film for the development of a DSSC. The surface morphological, structural, and optical properties of the fabricated layer have been studied using atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV-visible spectrophotometer. Power output characteristics like I-V characteristics and fill factor of the developed DSSC are also investigated.

2. Experimental

2.1. Preparation of CuS Thin Films. Substrate cleaning plays an important role in the deposition of thin films, because contaminated surface of the substrates results in the nonuniform film growth. Therefore, ITO-coated glass slides of the dimensions 15 × 10 × 1 mm were cleaned in an isopropyl alcohol using ultra bath sonicator for about 10–15 minutes and subsequently washed with distilled water. Later, substrates were dried in an oven at 100°C.

The thin film of CuS is fabricated by CBD technique [7, 24]. Copper sulphate [CuSO₄·5H₂O] (99.9% Merck), thiourea [SC(NH₂)₂] (99.9% Sigma Aldrich), triethanolamine [N(CH₂CH₂OH)₂] (98% SDFCL), and ammonia solution of analytical grade were used as received. Aqueous solution of copper sulphate, thiourea, and triethanolamine were prepared separately using double-distilled water before the experiment. 0.1 M CuSO₄·5H₂O solution was taken in a beaker; other ingredients such as 1:1 triethanolamine of 2.5 mL, 1 M thiourea of 5 mL, and 5 mL of 30% ammonia solution (NH₃) were added slowly one after the other with constant stirring. The bath solution was diluted to 50 mL using double-distilled water. The triethanolamine serves as a complexing agent to chelate with copper ions. The deposition of CuS films is based on the slow release of Cu²⁺ and S²⁻ ions in the solution, which are then condensed on to the glass substrates [25]. The thiourea was used as a source for sulphide ions, and ammonia solution is used to maintain the pH of the bath at 11. The deposition of CuS thin film on glass substrate using suitable bath solution containing copper ions at 1.5 pH is also reported [26]. Here, previously cleaned ITO-coated glass slides were immersed vertically in the bath for 5 h at lab temperature (or 300 K) without stirring the solution during the deposition. After the deposition, the substrates were taken out and washed with doubly distilled water and annealed at 250°C for 2 h in a vacuum annealing chamber.

2.2. Cell Preparation. For fabrication of the complete cell, the adsorption of dye was carried out on the thin film of CuS immediately after annealing to avoid the rehydration of the thin films. The procedure reported by Reda and El-Sherbieny [27] is adopted here for the adsorption of the dye on CuS thin film. The CV dye solution purchased from Rankem is used as such. The ITO-coated CuS film was dipped in dye solution at room temperature for 12 h. After the complete adsorption of the dye, for the first time the carbon counter electrode was prepared by collecting the carbon soot on the ITO-coated conducting glass slide. This counter carbon electrode was placed over the CV dye-coated electrode, and the edges of the cell were sealed to complete the fabrication of DSSC. A redox electrolyte consisting of a mixture of iodide/triiodide in acetonitrile was injected using a syringe into the space between the two electrodes. A schematic representation of the cell is shown in Figure 1. The area of the cell was 1.5 cm² (i.e., 1 cm × 1.5 cm).

2.3. Thin Film Characterization. For the analysis of particle structure, X-ray diffractometry (XRD) was conducted using Bruker AXS model D8 Germany. The structural property of the film was investigated by X-ray diffraction using CuKα radiation of wavelength (λ) = 1.5406 Å. Surface morphology was observed using Phenom scanning electron microscope (SEM). The surface of the film was examined by an atomic force microscope (AFM, PARK system). The AFM was operated in tapping mode to avoid destruction due to the use of a standard silicon tip. Optical properties were studied by measuring absorbance of the film using Shimadzu spectrophotometer within the wave length range of 320–1100 nm. The power output characteristic of a developed cell was studied by using the lab-equipped I-V measurement system. The measurements of current and voltages were in μ-amps and millivolts, respectively.

3. Results and Discussion

3.1. Surface Morphology of the Thin Film. The scanning electron microscopy (SEM) obtained for the fabricated thin film of CuS is shown in Figures 2(a)–2(d). SEM is a promising technique for the study of morphology of thin films. It gives important information regarding growth, shape, and size of the particles. Figures 2(a)–2(d) show the SEM micrographs obtained at different magnifications before and after adsorption of CV dye on CuS thin film. It is observed from Figures 2(a) and 2(b) that the grains are relatively good, compact,
homogeneous, and uniformly covered. It is to be noted that before the adsorption of CV dye, the particles are spherical and uniformly distributed whereas after the adsorption of dye on the thin film, cluster formation is observed as shown in Figures 2(c) and 2(d). This may be due to aggregated CV clusters.

An atomic force microscope (AFM) was used to study the surface morphologies of the CuS film fabricated on the ITO-coated glass substrate. It gives the particle size, structure, thickness, and surface roughness. This technique is capable of mapping three-dimensional images of the surface. Figures 3(a) and 3(c) are the two-dimensional (2D) images whereas Figures 3(b) and 3(d) correspond to 3D images of CuS thin film before and after dye sensitization. From the AFM image, it is found that these thin films are uniform, without cracks and consists of spherical nanosize particles which are well adhered to the substrate. The thickness of the film is found to be 250 nm. After CV dye adsorption the AFM pictures obtained were blurry. We believed that this is because the CV molecules were accumulated into clusters. The root mean square (rms) roughness is defined as the standard deviation of the surface height profile from the average height and is the most commonly reported measurement of surface roughness. The surface rms roughness of the film is 30 nm, and this roughness is unavoidable since the particles are spherical in shape. The observed rms roughness deviates from the reported value which may be due to various reasons like deposition time, solvent used, anisotropy of surface energy, and so forth [28, 29].

3.2. Structure Characterization. The XRD patterns obtained for the synthesized CuS thin film on glass substrate are as shown in Figure 4. The patterns show well-defined peaks suggesting that the film is crystalline. A comparison of the observed peaks of CuS at 2θ positions indicates the typical Covellite structure [7] whereas the presence of secondary phase of Cu₉S₅ is also indicated in the figure, and the planes which corresponds to these diffraction angles are closely corresponding to Deginite structure [30, 31].
The average size of the particles can be calculated from the full width of half maximum (FWHM) values of the diffraction peaks using Debye-Scherrer formula [32]

\[
D = \frac{0.94\lambda}{\beta \cos \theta},
\]

where \(D\) is the average crystallite size, \(\lambda\) the X-ray wavelength of CuK\(\alpha\) radiation (0.154 nm), \(\theta\) the diffraction angle, and \(\beta\) the FWHM. The size of the nanoparticle estimated at \(2\theta = 32.26^\circ\) from (1) is 2.38 nm. This indicates that the crystallite size is very small. The corresponding XRD data, that is, interplanar distance “\(d\)”, relative intensities, and calculated particle sizes are presented in Table 1. When the particle size is very small, appreciable broadening in X-ray diffraction lines will occur, and this depends on the particle size and strain [32]. Intensity of the peaks obtained here is much higher compared to the XRD pattern reported elsewhere, and the calculated average particle size is 19.7 nm for CuS, which is comparable with the average grain size of In\(_2\)Se\(_3\) [33].

3.3. Optical Characterization of the Film. Figure 5 shows the absorption spectra of CuS thin film before and after sensitization by CV dye. The absorption spectrum for CuS thin films was recorded in the wavelength region from 320 nm to 1100 nm. The deposited CuS thin films are having high absorbance in the UV region and low absorbance in the visible region as it can observe from UV spectrum before dye adsorption and a broad absorption peak located at nearly 430 nm to 700 nm in the visible region after the adsorption of CV dye on the CuS. The absorption edge of CuS is between 450 and 550 nm; after the dye sensitization it is shifted to 670 nm. An absorption edge corresponds to an electron excited by a photon of energy, whereby electron can jump from a lower energy to a higher energy state. However after dye sensitization, high absorption is shown by CuS thin film in the visible region, and also indicates the red shift. This shift
Table 1: The grain size calculated from Debye-Scherrer formula.

<table>
<thead>
<tr>
<th>Angle (2θ)</th>
<th>d (Å)</th>
<th>Intensity (counts)</th>
<th>FWHM of peak (β) in degrees</th>
<th>Size of the particle (D) in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.03</td>
<td>3.18</td>
<td>604</td>
<td>0.5128</td>
<td>17.87</td>
</tr>
<tr>
<td>32.26</td>
<td>2.77</td>
<td>1657</td>
<td>3.4874</td>
<td>2.38</td>
</tr>
<tr>
<td>37.20</td>
<td>2.41</td>
<td>76.8</td>
<td>0.2468</td>
<td>34.84</td>
</tr>
<tr>
<td>46.37</td>
<td>1.95</td>
<td>259</td>
<td>0.5370</td>
<td>16.40</td>
</tr>
<tr>
<td>54.83</td>
<td>1.67</td>
<td>54</td>
<td>0.2665</td>
<td>26.76</td>
</tr>
</tbody>
</table>

in absorption edge is maybe due to quantum confinement effects [27]. This helps DSSC to trap the photon energy in the entire UV–VIS spectral region.

The optical band gap \( (E_g) \) of the prepared CuS was calculated by using the relation [34, 35]

\[
(\alpha h\nu) = a(h\nu - E_g)^n,
\]

\[\alpha = 2.303 \frac{A}{\lambda}, \quad \text{(3)}\]

Figure 6: \((\alpha h\nu)^2\) versus \(h\nu\) plot of CuS thin film obtained by CBD technique on ITO coated glass substrate.
where $A$ is the absorbance and $t$ is the thickness of the film. The $(\alpha h)^2$ is plotted as a function of photon energy ($h\nu$) is shown in Figure 6. It varies almost linearly with photon energy above the band gap energy ($E_g$). Thus, (2) can be applied for a direct interband transmission [37]. The linear extrapolation of this curve to the energy axis gives the value of band gap of CuS thin film as 2.8 eV which closely agrees with the reported value [7].

3.4. Photovoltaic Measurements. The power output characteristics for a DSSC having the configuration: dye-sensitized CuS/iodide electrolyte/carbon electrode, was studied under illumination using halogen light source at lab temperature. The illuminated area is 1.5 cm$^2$. The open circuit voltage ($V_{oc}$) is 440 mV and short circuit current ($I_{sc}$) is 22 $\mu$A which were measured for the device under illumination. These are the critical parameters required for the calculation of solar cell efficiency. The microamperemeter does not play any role at the time of short circuit current measurement, and voltmeter does not play any role at the time of measurement of open circuit voltage. By changing the variable resistance the current and voltage were measured. Figure 7 is obtained by plotting the current density versus voltage.

The power conversion efficiency of the cell was calculated using (4), where $P_{in}$ is the incident intensity of light and FF is the fill factor

$$\eta = \frac{I_{sc} \times V_{oc} \times FF}{P_{in}} \times 100. \tag{4}$$

The maximum power output of the cell is given by the largest rectangle that can be drawn inside the curve. The fill factor (FF) is calculated using (5), where $I_{mp}$ and $V_{mp}$ are the current and voltage, respectively, for the maximum power output. The values of $I_{mp} = 9.6 \mu A/cm^2$ and $V_{mp} = 180 mV$ (cf. Figure 7)

$$FF = \frac{I_{mp} \times V_{mp}}{I_{sc} \times V_{oc}}. \tag{5}$$

The calculated values of fill factor and power conversion efficiency for the device are 27.1% and 0.34%, respectively. The result obtained indicates that the prospects are good for using organic dye as a photosensitizer in DSSCs. The power conversion factor for similar type of dye-substituted photovoltaic device in presence of $C_{60}$ [38], for dye-sensitized ZnS cell [39], is low when compared with our value reported here. However, photo properties of this device are not comparable with other sensitized solid-state devices [40–42]. Poor performance of this may be due to inefficient charge separation at the photo electrode-electrolyte interface, or the photo-generated electrons may leak out into the electrolyte instead of flowing through the external circuit results in low fill factor.

4. Conclusions

CuS thin films were successfully deposited on ITO-coated glass substrate by CBD, and it was used to fabricate a dye-sensitized CuS solar cell. The SEM images show that the deposited thin film has uniform grain size and compact. The AFM measurements have shown that the CuS thin film has high roughness. The deposited thin film is homogeneous, uniform, well adhered, without any cracks, and covers the entire substrate surface area. The XRD patterns obtained confirm the Covellite structure to be the main phase in the CuS thin film which would be preferable for the fabrication of solar cells and also indicate the presence of secondary phase of Cu$_2$S, which closely corresponds to Degenerate structure. Even though SEM and AFM show that the particle size of CuS is more than 1 $\mu$m, the average crystallite size (D) of CuS was found to be 19.7 nm. It is due to the fact that each solid compact cluster is made of number of particles having diameter in the range of nanometer. Optical measurements revealed a red shift in the absorption spectrum, which may be due to quantum confinement effects. Further, it helps to trap more photon energy in the UV-VIS region. Optical studies revealed that the film has direct allowed transition with band gap of 2.8 eV. The results obtained from photovoltaic measurements showed the short circuit photocurrent density of the cell made from dye-sensitized CuS. This film was found to be 14.5 micro amperes, and fill factor and efficiency of the developed DSSC will be 27.1% and 0.34%, respectively. Even though there are many other known solar cells with high efficiency, still the dye-sensitized solar cells find much importance in photovoltaic devices due to the fact that this chemical method can be utilized for the production of CuS in large scale at very low cost.

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References


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