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Deposition of copper iodide thin films by chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) methods

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ABSTRACT

In this paper, we report structural, morphological, electrical studies of copper iodide (CuI) thin films deposited onto glass substrates by chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) methods. CuI thin films were characterized for their structural, morphological and wettability studies by means of X-ray diffraction (XRD), FT-Raman spectroscopy, scanning electron microscopy (SEM), optical absorption, and contact angle measurement methods. Thickness of thin films was 1 ± 0.1 μm measured by gravimetric weight difference method. The CuI thin films were nanocrystalline, with average crystal size of ~60 nm. The FT-IR study confirmed the formation of CuI on the substrate surface. SEM images revealed the compact and cube like structure for CuI thin films deposited by CBD and SILAR methods, respectively. Optical absorption study revealed optical energy gaps as 2.3 and 3.0 eV for CBD and SILAR methods, respectively. Wettability study indicated that CuI thin films deposited by SILAR method are more hydrophobic as compared to CBD method.

1. Introduction

Copper iodide (CuI) is a water insoluble solid with three crystalline phases α, β and γ. Above 665 K, α-phase of cubic structure is a mixed conductor, where the charge carrier is predominantly Cu^{2+} ions. The hexagonal β-phase is also an ionic conductor. The low temperature γ-phase (below 623 K) is again of cubic structure. The CuI films are electrically conducting and optically transparent in the visible region of the solar spectrum with optical band gap values about 2.3–3 eV [1]. Due to these properties, CuI thin films are used as a buffer layer in solar cells. The basic requirements for buffer layer in solar cell are: (i) large energy band gap for high optical transmission in the visible region, (ii) optimal band discontinuities, and (iii) low lattice mismatch at the junction. Considering above requirements, the CuI has a band gap of 3.0 eV greater than traditional CdS material ($E_g = 2.4$ eV) and transmit higher energy photons, and CuI has a better lattice-matching to $CuInS_2$ thin film absorbers than CdS [2]. Further, from the point of environment safety, the establishment of a Cd-free process is significantly desirable in order to eliminate the Cd-containing waste discharged from the chemical deposition process [3]. CuI thin film deposited by thermal evaporation is used for synthesis of copper nanowires [4,5]. Electrical and optical properties of CuI thin films deposited by RF–DC coupled magnetron sputtering technique were studied by Tanaka et al. [6]. CuI deposited on copper substrate was p-type [7].

Konovalovi [8] studied the material requirements for p-CuI/n-$CuInS_2$ type solar cells and found that this material combination should be rather beneficial for solar cells since there was virtually no valence band offset. Verschraegen and Burgelman [9] found that the spike height and the spike width in CuI/$CuInS_2$ interface were determined by CuI doping concentration. For large-scale application, CuI was used as a buffer layer on n-CIS absorber in CIS/CuT based solar cells manufactured in a roll-to-roll process. A device efficiency of 9.2% was achieved [10].

The synthesis of thin films by chemical methods is simple, less expensive, and convenient for large area deposition as compared to other physical methods. Chemical methods are simple, economic and convenient for the deposition of metal oxides, metallic chalcogenides and polymer thin films. The preparative parameters such as concentration, pH, nature of the complexing agent, temperature etc are easily controllable. Chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) are two chemical methods used for synthesis of CuI. In addition, SILAR method take less time as compared to CBD for synthesis of film so it is used to deposit compound materials on a variety of substrates

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such as insulators, semiconductors, metals [11]. Further, CBD and SILAR methods are employed by Sankapal et al. [12] to obtain the CuI and CuSCN thin films for solar cell windows application.

In this paper a comparison of physical properties of CuI thin films deposited by CBD and SILAR method is made. In order to find the suitable method for the deposition of CuI thin films, CBD and SILAR methods are used for preparation of CuI thin films and comparing physical properties of these films are studied.

2. Experimental details

2.1. Preparation of copper iodide thin films

I) CBD method:

The CuI thin films are deposited on glass substrates. The chemicals used were of AR grade. The chemical bath was prepared using 0.5 M solution of copper sulfate and added into 0.5 M potassium iodide drop-wise at room temperature upto the formation of precipitation. The precipitate of CuI is washed with hot water, followed by acetone and dried in vacuum at 353 K for 1 h to remove residual iodine. The solubility of CuI in acetonitrile enabled us to devise the following simple method for coating thin optically transparent films of CuI on glass substrate. 0.70 g of CuI was dissolved in 50 ml of moisture free acetonitrile and a cleaned glass substrate was dipped into the solution. After 15 h, CuI film was taken out from bath having maximum thickness 1 ± 0.1 μm. This film was used for further characterization.

II) SILAR method:

Fig. 1 shows schematic of SILAR deposition method, in which beaker 'A' consists of an aqueous solution of 0.1 M $CuSO_4$ as a cationic precursor and 0.1 M $Na_2S_2O_3$ solution of pH ~5 acts as a the reducing agent as well as the complexing agent. The reaction with iodine was achieved in beaker 'C' using 0.025 M KI solution of pH ~6 as an anionic precursor. The beaker 'B' and 'D' with distilled water were used for rinsing purpose. The film thickness of 1 ± 0.1 μm was obtained after 35 cycles.

2.2. Characterization techniques

The structural characterization of CuI thin films was carried out by analyzing X-ray diffraction (XRD) patterns obtained with CrK_α ($\alpha = 2.2897$ Å) radiation from a Philips X-ray diffractometer model PW-1710 in the span of angle 10–100°. The FT-Raman spectra of the films were recorded in the spectral range of 100–3400 cm^{-1} using model FT-Raman Multi RAM Brukar. The surface morphological analysis was done using scanning electron microscopy (SEM) JEOL JSM model 6360. The wettability of the film was carried out by Rame-hart USA equipment with CCD camera. The optical absorption study was done within a wavelength range CuI 300–850 nm using a UV-1800 SHIMADZU spectrophotometer. The electronic conductivity of CuI thin films was determined by two-probe method. The tin contact was prepared using vacuum coating unit of HIND HIGHVAC before conductivity measurement.

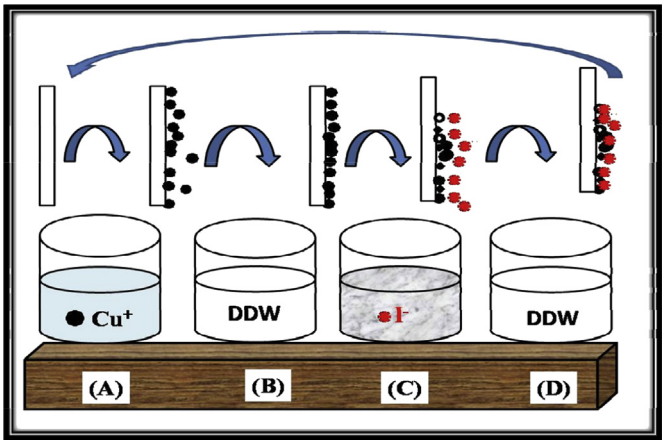

Fig. 1. The schematic of successive ionic layer adsorption and reaction (SILAR) method beaker (A) contains 0.1 M $CuSO_4$ and 0.1 M $Na_2S_2O_3$, beaker (B) contains distilled water, beaker (C) contains 0.025 M KI and beaker (D) contains distilled water.

3. Results and discussion

3.1. Copper iodide (CuI) film formation

The reaction mechanism of the formation of copper iodide is as follows

I. CBD method:

We used an aqueous solution bath at room temperature consisting of 0.5 M $CuSO_4$ with pH ~5. The release of Cu^{2+} ions is possible via the following reaction:

$$CuSO_4 \rightarrow Cu^{2+} + SO_4{}^{2-}, \quad (1)$$

$$Na_2S_2O_3 \rightarrow 2Na^+ + (S_2O_3)^{2-}. \quad (2)$$

In this reaction, $Na_2S_2O_3$ acts as both the reducing agent as well as the complexing agent. $Na_2S_2O_3$ reduces the Cu^{2+} to Cu^+.

$$[Cu(S_2O_3)] \leftrightarrow Cu^+ + (S_2O_3)^-. \quad (3)$$

This acts as a source of cations. The reaction with iodine was achieved using 0.5 M KI with pH ~6 of solution.

$$KI \rightarrow K^+ + I^-, \quad (4)$$

$$Cu^+ + I^- \rightarrow CuI. \quad (5)$$

The film is formed on the substrate and precipitate is formed in the chemical bath. The above reaction was carried out at room temperature.

II) SILAR method:

Fig. 1 shows the schematic of SILAR method for the deposition of CuI thin film, where the beakers represent (A) cationic (Cu^+) precursor, (B) distilled water, (C) anionic (I^-) precursor, and (D) distilled water. We used an aqueous solution bath consisting of 0.1 M $CuSO_4$ with pH ~5 and 0.1 M $Na_2S_2O_3$ which forms thiosulphatocuprate (I) complex [6]. The release of Cu (I) ions is possible as reaction (3).

This acts as a source of cations. The reaction with iodine was achieved using 0.025 M KI with pH ~6 solution. The substrate was immersed in a cationic precursor for 5 s. Copper ions were adsorbed on the surface of the substrate and the un-adsorbed ions were removed by rinsing the substrate in distilled water for 5 s. For the reaction with I^- ions, the substrate was immersed in an anionic