Section A-Research paper

Synthesis of Cu_2S Thin Films by Arrested Precipitation Techniques: A Novel Approach

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Abstract

Nanogranular thin films of copper sulfide (Cu_2S) deposited by self-organized Arrested Precipitation Technique. The deposited Cu_2S films were characterized for optical, structural, and morphological properties. Optical absorption study suggested the band gap energy decreased from 2.91 to 2.26 eV with increasing precursor concentration. X-ray diffraction results indicate that APT is a favorable technique to synthesize pure nanocrystalline Cu_2S thin films having a monoclinic crystal structure. An electrochemical impedance spectroscopy analysis confirms the charge transfer resistance and electron lifetime. X-ray photoelectron spectroscopy reveals stochastic at valance state of Cu_2S.

Keywords: *Arrested precipitation technique, Thin films, Band gap, and PEC*

1. Introduction

Recently nanotechnology-enhanced thin film solar cell is a promising and potentially important emerging technology [1], designing stochastic nanoscopic inorganic semiconductor coatings will be better alternatives for the depletion of energy sources, such as fossil fuels, natural gas, and coal oils has led to the fabrications of new energy sources [2]. However, most of the semiconductor solar cell suffers from photo corrosion with the I^-/I_3^- redox couple, and the polysulfide mediator chemisorbs on the platinum surface and induces poisoning effects on the electrochemical performance [3]. Hence copper containing chalcogenides compound semiconductors focused on the as extremely thin absorber layers [4], counter electrodes like Cu_2S [5] and CuSe [6].

Metal chalcogenide thin film materials can flexibly deposit on substrates such as glass, plastic, especially suitable for solar building integration as optoelectronic devices, and PEC solar cell devices [6], due to easy junction formation with redox mediator [7]. The increasing popularity of IB-VIA, and II-VIA group chalcogenides is their high absorption coefficient in visible radiation and electron-hole separations during the working of solar cells [8]. Copper sulfide (CuS, 2.9 eV) [9] shows the materials are visible radiations active and semiconducting. But they lack generality or need sophisticated instrumentation, and are complicated due to the synthesis of copper chalcogenide materials with toxic reducing agents, surfactants, solvents, and high temperature [10]. Hence the solution-processed synthesis using APT method is simple, and cost-effective [11], that has comparable structural, compositional, and opto-electrical properties over other sophisticated deposition techniques [12].

In the present investigation, we have selected amino alcohol (TEA) as a polydentate ligand and forms a complex with copper metal ions to arrest the bulk precipitation. The invention in this report is to optimize the growth mechanism conditions especially reduction of copper metal ions due to mild reducing agents (Na_2SO_3) and form uniform highly adherent nanogranular surface morphology of Cu_2(S, Se) (abbreviated as CSSe) thin films at ambient temperature. Stochastic CdSSe thin film deposited using the APT, confirms by using the XPS and applied to PEC response.

APT is a hybrid chemical bath deposition method in combination with the controlled chemical growth process (CCGP) for chemosynthesis of ternary nanoalloys [11]. Thus, smaller crystallites serve as nutrients to the directional larger growing crystallites in inorganic metal chalcogenide coating thin films [13]. The most significant advantages described here of ternary CSSe thin films as counter electrode for CdSSe thin film solar cell. To the best of our knowledge, there is no particular report available on the novel chemosynthesis of CSSe thin films using TEA as a surface-active growth controller. The obtained results are comparatively better than those of as reported efficient counter electrodes alternative to platinum [5-6].

2. Materials and method

2.1 Experimental details

All the chemicals were used are analytical reagent (AR) grade without further purification. Copper sulfate pentahydrate ($CuSO_4$ $5H_2O$) (98 %, S-D Fine Chem.), Thiourea ($H_2N–CS–NH_2$) (99 %, S-D Fine Chem.), Ammonia solution (NH_3) (30 % Thomas Baker), and Triethanolamine (N $(CH_2CH_2OH)_3$) (99 %, Merck) were used as precursors and TEA as growth controller. The substrates were cleaned with the chromic acid solution heated at 50^0C for 5 min, then ultrasonically cleaned using isopropanol and demonized water mixture. Herein, Cu_2S thin films were deposited on bare glass substrates by facile technique.

2.2 Synthesis of Cu_2S thin films

In a current synthetic pathway, we addressed simple chemical reactions. 0.03 - 0.05 M copper sulfate solutions were used for formation of a complex with the amino alcohol (TEA) as a polydentate ligand to obtain the clear transparent solution. The Cu^{2+}–$(TEA)_2$ complex reacts with the S^{2-} chalcogen ions with slow release via dissociation of $H_2N–CS–NH_2$ at alkaline pH=10.5. The deposition of Cu_2S thin films was achieved by using the nucleation and Ostwald's ripening mechanism. These mechanisms are mainly dependent on the different preparative parameters such as concentration of ligands, Cu^{2+} precursor concentration, pH, deposition time, single-solution phase, agitations speed (RPM) and temperature of the bath. Hence, all these parameters were optimized during the initiative stage of thin film deposition. The precursor concentration varies from 0.03 - 0.05 M Cu^{2+} and the deposition time, ambient temperature, (RPM) were fixed. After formation of the Cu_2S films, thickness of the film was measured using a surface profiler. The increasing concentration of Cu^{2+} precursor demonstrates the rapid growth of the films, the film thickness will be increased. Once depositions are over, the peeling of the substrate with an overgrown surface, without an increase in film thickness was observed. Hence, we have studied the effect of Cu^{2+} precursor concentration on deposition. In the terminal growth phase, all the deposited thin films were uniform, strongly adherent transparent blackish colored and correspondingly designated as, C1, C2 and C3.

2.3 Characterizations

Optical absorption spectra were recorded using a UV-Vis-NIR spectrophotometer (Shimadzu, UV-1800). The thickness of the deposited thin films was measured using a surface profiler (AMBIOS XP-1). Structural properties were confirmed using an X-ray diffractometer (XRD) (Bruker AXS, D8) using Cu Kα (λ = 1.5418 Å) radiation for 2θ ranging from 20 to 80^{o}. The surface morphology and the elemental composition of the deposited thin films were demonstrated using field-emission scanning electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Multilab-2000) with a multi-channel detector, which can endure high photon energies from 0.1 – 3.0 keV. The surface adsorption was studied by using a BET analyzer (Quantachrome Instruments). EIS was performed by using the auto lab PGSTAT 100 FRA 32.The infrared spectrum demonstrated by using the FT-IR.

3 Results and Discussion

3.1 Growth mechanism of thin films formation

To understand that shape evolution processes are predictable, it could be possible to investigate properties of deposited material with desired morphology and crystallinity. In the present technique, Cu^{2+} metal ions are complexes using complexion (TEA) and are slowly released at the optimized precursor concentration, pH, and temperature. Aqueous ammonia is used to optimize the pH, by increasing the concentration of the OH^- ions, the relative increase in releasing ability of the chalcogen ions (S^{2-}) in the reaction solution [11]. However, at a higher temperature, s metal ions released rate increases and reaction proceeds rapidly causing bulk precipitation instead of the desired quality thin film formation. So, we have to first optimize the depositions at ambient temperature (300^o K), Cu^{2+} precursor concentrations (0.03-0.05 M), and pH=10.5. The high-quality, uniform Cu_2S thin films were synthesized. Nucleation and Ostwald ripening mechanism is base of APT techniques. In ambient temperature, an increase in Cu^{2+} precursor concentration (0.03 - 0.05 M) the desired quality of film obtained due to optimized reaction rate, which favors the smaller particles and the formation of well-grown stable crystals. The deposition of the thin films occurs when the ionic product (K_p) exceeds the solubility product (K_{sp}) of the metal ions. The nucleation process occurs next to the ion-by-ion condensation of the metal ions onto the substrate surface [11]. Generally, a slow reaction rate results in the formation of excellent stoichiometric compositions with high-quality and adherent thin films [15]. Hence, hybrid developed arrested precipitation technique is effective compared with routine chemical bath processes.

3.3 Optical studies

Fig. 1 (a) UV-Vis-NIR spectrophotometer shows the wavelength range 300 – 900 nm, the optical absorption spectra of the Cu_2S thin films recorded and clearly shows that the maximum visible radiations absorption is observed at around 400–550 nm. The enhancement in the absorption is due to the considerably improved thickness and decreasing band gap value of Cu_2S thin films. An absorption coefficient value of all samples is found to be order of $10^5 cm^{-1}$. The electron excitation from the valance band to the conduction band can be used to determine the value of the optical band gap energy. Optical data here signifies using the equation (10)

$$\alpha = \frac{A\left(h\nu - E_g\right)^n}{h\nu} \quad \text{……………………………………} \quad (10)$$

where A is a parameter that depends on the transition probability, h is the Planck constant, Eg is the optical band gap energy of the material, and the exponent (n) depends on the type of transition. The values of (n) for the direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions are 1/2, 2, 3/2 and 3 respectively.

The linear increase in absorption intensity with decreasing the band gap energy (eV) with increase in thickness of film suggests a direct and allowed type of transition. The band gap energy decreases from 2.91 – 2.26 eV with increase in Cu^{2+} precursor concentration (0.03 - 0.05 M), due to the uniform compact nanogranular thin films. The optical band gap energy values of the Cu_2S thin films were obtained by plotting the graph (b) of $(\alpha h\upsilon)^2$ $(eV/cm)^2$ Vs $(h\upsilon)$ (eV) as shown inset of Fig. 1. The obtained optical band gap values resemble with reported values [10]. Variations of thickness, band gap (E_g) with a concentration of copper are depicted in Table 2.

3.4 X-ray diffraction (XRD) for structural studies

The crystal structural analysis and nature of samples were recorded by X-ray diffraction pattern in the range 2θ of 20^o to 80^o. Fig. 2 Shows the X-ray diffraction pattern of the Cu_2S thin films. XRD pattern shows the broad, intense peaks in all the samples deposited at different concentrations of precursors and confirms that the Cu_2S thin films are pure nanocrystalline by nature [16]. The major diffraction peaks centred at 2θ values 27.44, 43.82, 51.34, 51.81, 54.44 A^o and can be indexed as (111), (220), (311), (311), (222) for cubic crystal system. The experimentally calculated values are good agreement with JCPDS card no.79-1841, 84-1770 and indicate quality of crystal structure.

In a typical X-ray diffraction analysis of the Cu_2S thin films, peaks appear at identical positions with amendments to the intensity and broadening the diffraction peaks, which indicates the creation of pure phase materials with an improved crystallinity with increasing thickness of the film. Some of the small intensity peaks reveal the nature of the films amorphous due to glass beads are presents with materials. In addition, no other peaks are observed which reveals that the material has a pure phase. The observed broadening of the diffraction peaks may be due to strain or micro-strain. Further, the crystallite size was calculated using the Debye Scherer formula equation (11) [16].

$$D = \frac{0.9\lambda}{\beta \cdot \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(11)}$$

Where D is the crystallite size, λ is the wavelength of X-ray radiation (1.5406 Å), β is the full-width-at-half-maximum (FWHM) in radians, and θ is Bragg's angle. The calculated crystallite size is improved from 22-34 nm with concentration. This crystallite size with the minimum interfacial energy is beneficial for improving the photon conversion efficiency [17–19]

3.5 Fourier transform infrared spectroscopy (FT-IR)

The typical FT-IR spectrum confirms the formation of the pure C3 thin film. The band at particular positions with its stretching frequency values are shown in Fig. 3. FT-IR spectrum recorded at range 400 - 4000 cm^{-1} shows the peak at stretching frequency 1134, 2330, 2900 & 3100, 3471 cm^{-1} are related to the CuS, CN, CH, NH_2 [20]. Although some other peaks are also present due to the surface contamination, remain at a lower proportion [21].

3.6 Nitrogen adsorption and desorption isotherm study

The specific active surface area and porosity of the C3 nanograins were evaluated by using the Brunner, Emmett and Taylor (BET) isotherm and as shown in Fig.4. Typical isotherm reveals the adsorption and desorption branch of type II and IV pattern, indicating the presence of micro with mesoporous material having a three dimensional (3D) intersection classification [22]. It confirms the formation of a multilayer along with monolayer adsorption and desorption hysteresis loop. The surface area of nanogranular thin films is 30.840 m^2/g as shown in Fig.4. This result indicates that the synthesized material has a wider micro-mesoporous structure. The pore radius of 1.8 nm was investigated by desorption branch of the BJH method. This kind of good quality of the candidate for a solar cells can be selected on the basis of the increasing the surface area, pore radius respectively, Hence C3 type of mesoporous structure can be useful for efficient electrolyte diffusion into the electrode in semiconductor solar cells [23].

3.7 Electrochemical impedance spectroscopy (EIS)

EIS was employed to study the PEC kinetics of the Cu_2S thin films. In order to study the effect of concentration on conversion efficiency. EIS measurements were conducted in dark using the 0.2 M polysulfide mediator with applied forward bias voltage - 0.5 V. The measuring ac frequency range was 0.1 Hz to 1000 Hz Fig.5 (a) Shows the Nyquist plot of Cu_2S samples, the equivalents circuit fit the spectra are shown inset of Fig.5 (a). Various parameters obtained for Cu_2S thin films from circuit are listed in Table 2. The solution resistance (Rs), R_1 is the charge transfer resistance between the Pt-FTO counter/electrolyte interface and charge transfer resistance (R_2) related to photo-excited electron hole recombination at Cu_2S/mediator. The electron lifetime (τ_e) value calculated by using formula shown in Eqn.(12), [24] also indicates the electron hole recombination during the PEC operation and obtained from bode plot Fig. 5 (b). From these results we can conclude that electron lifetime increases and the recombination decreases with increase in thickness.

$$\tau_e = \frac{1}{2\pi f} \qquad \text{.......................................} \quad (12)$$

3.8 Morphological studies

Field-emission scanning electron microscopy (FE-SEM) demonstrates the surface morphology of Cu_2S thin films. Fig. 6 Shows the FE-SEM micrograph of the Cu_2S thin films at low and high magnification with the various concentrations of the precursors. The FE-SEM micrographs demonstrate that uniform, nanogranular thin films were deposited over the entire surface. Fig. 6 (a) and (b) show the FE-SEM images for the Cu_2S thin film deposited at 0.03 M. A beaded nanogranular-like morphology was obtained at a lower concentration of the precursors. The growth of the Cu_2S materials with the small grain size shown in lower concentration and are arranged over the entire substrate surface. These nanogranular-like materials have a grain size of ~ 50 nm. Fig. 6 (c) and (d) show the FE-SEM images for the Cu_2S thin film deposited at 0.04 M. Nanograins are assorted to form the uniform morphology, indicated in Fig. 6 (c). From the higher magnification image Fig. 6 (d), it can be seen that the interlinked nanograins have a grain size of ~ 70 - 80 nm. The construction and aggregation of the assorted nanograins with the increase in thickness might be due to the increase in the concentration of the precursors with a slightly increasing rate of depositions. Fig. 6 (e) and (f) show the FE-SEM images for the Cu_2S thin film deposited at 0.05 M. A complete conversion from nanograins to the compact uniform film growth due to the increasing thickness of the films with increasing the concentrations Fig. 6 (e). The higher magnification image Fig. 6 (f) demonstrates that the nanograins are completely assorted with uniform grain size ~ 90 - 100 nm. The formation of complete uniform growth with assorted nanograins, is due to the aggregation of the nanograins. Schematic representation of the formation of the uniform nanogranular-like texture is observed to occur via the assembly of a large number of nanograins. These nanograins are assorted to obtain high surface area due to the interlinking. It is evident from schematic illustrations that the nanograins-like texture is reflected in the assorted nanograins. This type of nanogranular–texture reduces the charge transfer resistance and the photoelectrochemical performance increases.

3.9 Compositional analysis of Cu_2S

To confirm the surface elemental composition of the C3 thin film. The XPS survey and high-resolution core level spectrum demonstrated. The two prominent peaks confirm the presence of Cu, and S elements respectively. Furthermore, elements valance state and the existing form of the Cu_2S thin film was investigated by XPS study as shown in Fig. 7 (a), peaks along with C and O in the sample. The core level spectrum of copper Fig.7 (b) shows prominent peaks of Cu2p which can be distinguished, in which two peaks located at binding energies of 932.98 eV and 952.99 eV are assigned to Cu2p3/2 and Cu2p1/2, confirming the presence of Cu^+ in the sample. However, weak satellite shake-up peaks were also observed at binding energies around 942.3 eV. Moreover, two peaks with binding energies of 932.98 eV and 952.99 eV were assigned to Cu2p3/2 and Cu2p1/2, confirming the presence of Cu^+ with splitting energy of 20.1 eV [25] [26]. The core level spectrum of sulfur Fig. 7 (c) indicates two strong peaks at binding energies 160.65 eV and 161.9 eV are assigned to S3p3/2 and S3p1/2 respectively, which is consistent with the S^{2-} in sample with a splitting energy of 1.25 eV. However, the weak peak shown at 166.2 eV at core level indicates that the surface contamination with S^{2-} oxidation state (S2p1/2). The values of the binding energies for Cu, and S are at their respective positions for the Cu^+, and S^{2-} state. It means that Cu^+, and S^{2-} exists in the stochastic formula of deposited Cu_2S thin film.

4. Conclusions

Concisely, nanogranular Cu_2S thin films have been synthesized using single-solution phase arrested precipitation technique. The effect of Cu^+ ion concentration on the morphology has been studied systematically. Opto-structural and morphological studies reveal Cu_2S thin films have controls over the directional crystal growth due to crucial role containing TEA, tuning of band gap energy 2.92 - 2.26 eV. XRD pattern results the crystalline nature with pure monoclinic crystal structure, which controls the ion insertion kinetics leading to a charge transfer reaction. Stochastic Cu_2S thin film at chemical valance state is confirmed by XPS. BET study reveals that the nanograins have micro-mesoporous nature of the C3 sample with highest surface area of 30.840 m^2/g. It was demonstrated that the deposited Cu_2S counters have hold potential and exhibit good electronic properties for optoelectronic device fabrication.

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