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Low cost nanostructure kesterite CZTS thin films for solar cells application

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ABSTRACT

Nanostructure Cu_2ZnSnS_4 (CZTS) thin films were synthesized by Successive Ionic Layer Adsorption and Reaction (SILAR) method. The as-grown CZTS thin films have shown amorphous structure but after sulfurization at 450 °C temperature, CZTS thin films showed kesterite crystalline structure. The crystallite size of annealed CZTS thin films is to be ~18 nm and kesterite structure was confirmed by XRD pattern and Raman spectra show pure CZTS peaks at 337 cm^{-1} and 368 cm^{-1}. The FE-SEM images indicate the presence of small agglomerated grains & visible white pores of as grown and annealed samples. The direct band gap energy of CZTS thin films was decreased after annealing under sulfur atmosphere. CZTS thin films have suitable absorber material for solar cells confirmed by structural, optical and morphological properties. CdS quantum dot has been used as a window layer to deposit on Indium doped tin oxide (ITO) & Fluorine doped tin oxide (FTO) substrates for measured power conversion efficiency of CZTS material confirmed by J-V characteristics.

1. Introduction

The thin film solar cells are generally produced by using CdTe or CIGS based light absorbing materials. Unfortunately, these materials have several issues like toxicity and cost of the materials. Replacement of these materials by widely available, non-toxic and higher light absorbing materials is an immediate need. One of such material is CZTS which is cost effective, holds high absorption coefficient and has appropriate direct band gap for solar energy utilization [1]. Non-toxic CZTS material is one of the promising materials which can suitably complete all these requirements of absorber layer [2]. The CZTS is a quaternary semiconductor containing an appropriate optical band gap ~1.5 eV and sufficient absorption coefficient of 10^4 cm^{-1} for application in solar cells [3]. The synthesis of CZTS thin films was widely investigated and several techniques were proposed such as electrochemical technique, pulsed laser deposition, sputtering, evaporation, chemical vapor deposition, CBD, SILAR [4–10]. Some limitation and disadvantages of physical methods researchers focus on chemical methods [9]. SILAR method compared to CBD method has control reaction rate and thickness using Cations and anions over the substrate. SILAR method is low cost, easy for large scale production and requires low deposition temperature [10]. Suryawanshi et al. prepared CZTS thin film by SILAR method and annealed at 575 °C temperature for 1 h and got 1.81% highest efficiency [11]. Here, we annealed CZTS thin films at 450 °C temperature for 1 h to improve the efficiencies. Quantum dot has an excellent optical property such as narrow emission spectrum and tunable band size [12]. Researcher focus on different quantum dots semiconductor materials to use as a window layer in solar cells. CdS quantum dot has proved higher photocurrent response and it use buffer layer as well as window layer material in P-N junction solar cells [12].

In this work, we are reporting a comparative study of as grown and sulfurization of CZTS thin film by SILAR method. In particular, we have annealed CZTS thin films at high temperature i.e. 450 °C in the sulfur atmosphere. Furthermore, these as-grown and sulfurized

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thin films were examined for their structural, morphological, and optical properties and the results are reported. We have used CdS quantum dots as a window layer material to deposit on ITO and FTO substrates to improve and measure the power conversion efficiency of kesterite CZTS thin films.

2. Experimental

CZTS thin film was deposited on glass substrate by SILAR method at room temperature. CZTS thin films were deposited by using 0.05 M $CuCl_2$, 0.1 M $ZnSO_4$, and 0.05 M $SnCl_2$ as cationic precursor solutions. The proper amount of liquid ammonia was added to cationic precursor solutions to maintain pH at ~11. The sodium sulfate (Na_2S) is an anionic solution was separately prepared [13]. Cations and anions were deposited layer by layer on the surface of the glass substrate and after synthesis substrate was annealed under the vacuum condition in presence of H_2S (5%) + N_2 (95%) atmosphere at 450 °C for 1 h in two zones tubular furnace [11]. The nanostructured CdS thin film deposited on silicon glass substrate, ITO and FTO substrate by Chemical Bath Deposition (CBD) method. In this experiment, we took 0.5 M cadmium sulfate ($CdSO_4$) and 1 M thiourea ($SC(NH_2)_2$) as a source of Cadmium and sulfide respectively [14]. A few drops of ammonia added cadmium solution to control precipitation and stirrer few minutes. Then both solutions mixed together and heat at 60 °C for 60 min.

The structural properties of thin films were studied using X-ray diffraction (XRD) and Raman spectroscopy. The morphological studies of thin films were studied by Field Emission Scanning Electron Microscopy (FESEM). Optical properties such as absorbance and band gap were measured by UV–VIS spectroscopy. The photovoltaic characteristics were studied on ITO and FTO conducting substrates and measured by J-V characteristics method. The Physical vapor deposition instrument is used for deposit gold contact to measured power conversion efficiencies.

2.1. Solar cell device formation

We have used ITO and FTO sheet resistance 8 Ω/sq. glass substrates. First, we took two ITO & FTO glass substrates and deposited CdS thin film by CBD method. After synthesis, both CdS thin film annealed at 100 °C for 60 min. Second, CZTS absorber materials have deposited on CdS/FTO and CdS/ITO substrates by SILAR method. The devices annealed in the sulfur atmosphere at 450 °C [ITO/CdS/CZTS] and [FTO/CdS/CZTS] to improving crystallinity and compactness of the thin film. The gold contact used for measured power conversion efficiencies.

3. Results and discussion

XRD pattern of as-grown and annealed CZTS thin films on glass substrates were shown in Fig. 1(A). The XRD plots for the as-grown thin film confirmed an amorphous phase while sharp peaks were located at 28.16°, 32.50°, 37.49°, 47.52° and 56.48° after annealing in a sulfur environment corresponds to CZTS phase. Specifically, these peaks are originated from the (1 1 2), (2 0 0), (2 0 2), (2 2 0) and (3 1 2) planes respectively [13]. The main peak at 28.16° is narrow and sharp which indicates that CZTS thin film has kesterite structure. Consequently, annealed thin films under sulfur atmosphere certainly exhibit improved crystalline structure. The average crystallite size was estimated from the X-ray diffraction pattern using the Deby e- Scherer's formula and is to be ~18 nm [10]. Raman spectroscopy is an important technique used to find out diverse possible phases in the CZTS thin film. Fig. 1(A) shows inside inserted Raman spectra graph of sulfurized CZTS thin film. Raman spectra of the CZTS thin films were recorded in the range of 200–600 cm^{-1}. Sharp peaks at 337 cm^{-1} and 368 cm^{-1} were identified for thin film sample which is a characteristic feature of the kesterite CZTS structure [15]. However, Raman spectra exhibit a peak located at 266 cm^{-1} which are attributed to the Cu_2SnS_3 phase [15]. Fig. 1(B) shows the XRD spectrum of CdS thin film deposited on glass substrate. XRD analysis indicated that the film is polycrystalline with less intensity of peaks. The observed diffraction peaks at 26.61°, 29.58°, and 52.01° correspond to reflections from (1 1 1), (2 0 0) and (3 1 2) planes of cubic phase of CdS thin film [12]. The CdS thin film average crystallite size is to be ~8 nm and it confirmed quantum dot size or nanocrystalline structure [12].

In order to study the surface morphology, the thin films were examined by FESEM. Fig. 1(B) Shows the XRD spectrum of CdS thin film and inserted FESEM images different resolution at (a) 2 µm and (b) 500 nm. The slow deposition rate ~1 h to shows the small grain size and leaf-like shape has good adhesion to the substrate. CdS thin film has prepared by CBD method shows porous leaf-like morphology [12]. Fig. 2 show FE-SEM images at different resolutions of as-grown (a–c) and sulfurized (d–f) CZTS thin films. The as-grown thin films show voids with porous morphology and the low uniformity but sulfurized sample, shows that the morphology of the films is compact with enhanced homogeneity [13]. Also, the sulfurized samples have better surface quality than the as-grown samples.

The optical properties have been examined to study the light absorption properties and to estimate the band gap of the material. The absorbance spectra of the as-grown and sulfurized CZTS thin films were measured by the UV–Vis spectrophotometer in the wavelength range 400–1100 nm shown in Fig. 3(A). From Fig. 3 (A) it can be clearly seen that the optical absorption edge shifted to longer wavelengths after sulfurization process. The energy band gap values were calculated using Tauc's equation [16]. Fig. 3(A) the as-grown and sulfurized samples band gap values were 1.66 eV and 1.56 eV respectively. The annealing effect shows a decrease the band gap of CZTS which is in good agreement with their structural properties [13]. According to the band theory in the literatures about electronic transitions in CZTS material upper valence band (VB) is formed by hybridization between states and increase sulfur concentration by sulfurization [17]. Absorption in this energy range is completely dominated by transitions from the Cu t_{2g} orbital's hybridized with S-3 p states in the upper valence bands into the anti-bonding Sn-5 s/S-3 p$*$ band in the lower conduction bands [18]. Fig. 3(B) shows the CdS thin film has revealed the band edge in the visible range at wavelength ~515 nm and the band gap is to be ~2.4 eV [14].

Fig. 3(C) shows J-V characteristics curves of first sample ITO/CdS/CZTS and second sample FTO/CdS/CZTS thin films. Both heterojunction solar cells having 1.6 × 1.6 cm^2 dimension. The power conversion efficiency is calculated by following equation [19].

$$\eta(\%) = \frac{P_{max}}{P_{in}} \times 100 \tag{1}$$

where Pmax is maximum output power observed in the thin film, and Pin is the input power applied to the film surface and η is power conversion efficiency. The dark becomes surface region becomes negatively charged when exposure of light on the surface it becomes positively charged indicating the increased electron and hole density [20]. From Fig. 3(C) it can be seen that CZTS on ITO substrate gives a short circuit current density (*Jsc*) of 4.6 mA/cm^2, open circuit voltage (*Voc*) of 723.3 mV, fill factor (*FF*) of 0.51% and power conversion efficiency (η) of 1.68% under illumination condition. Sample ITO has enhanced *Voc* but efficiency decrease because the higher temperature it does not works [21]. FTO substrate works up to 500 °C temperature due to this reason improved the short cir-

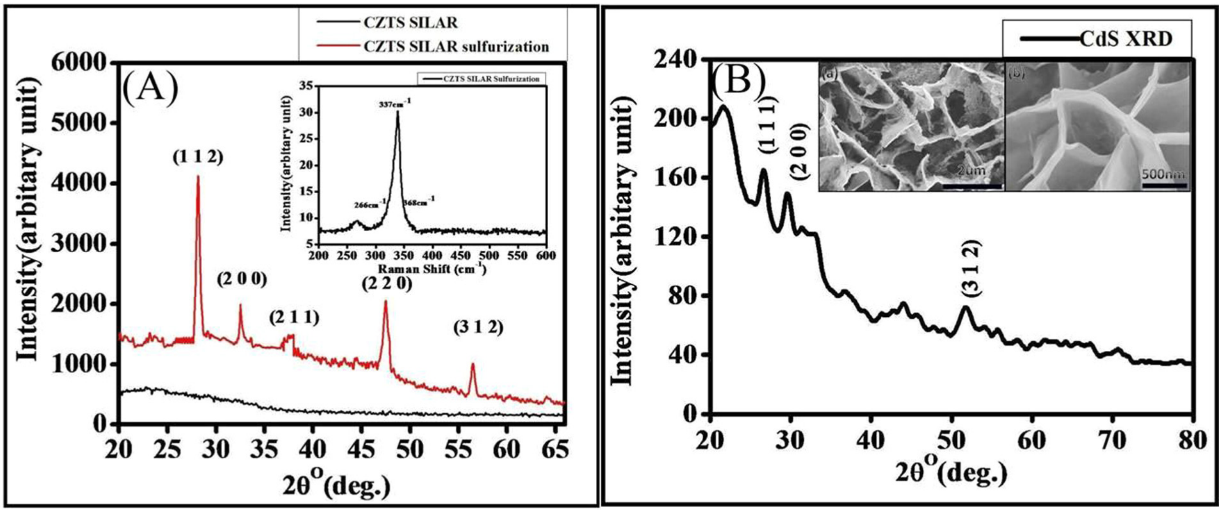

Fig. 1. (A) XRD patterns of as-grown and sulfurized CZTS thin films grown by SILAR and inserted sulfurized Raman spectra; (B) XRD patterns of CdS thin films and inserted FESEM images (a) 1 μm (b) 500 nm.

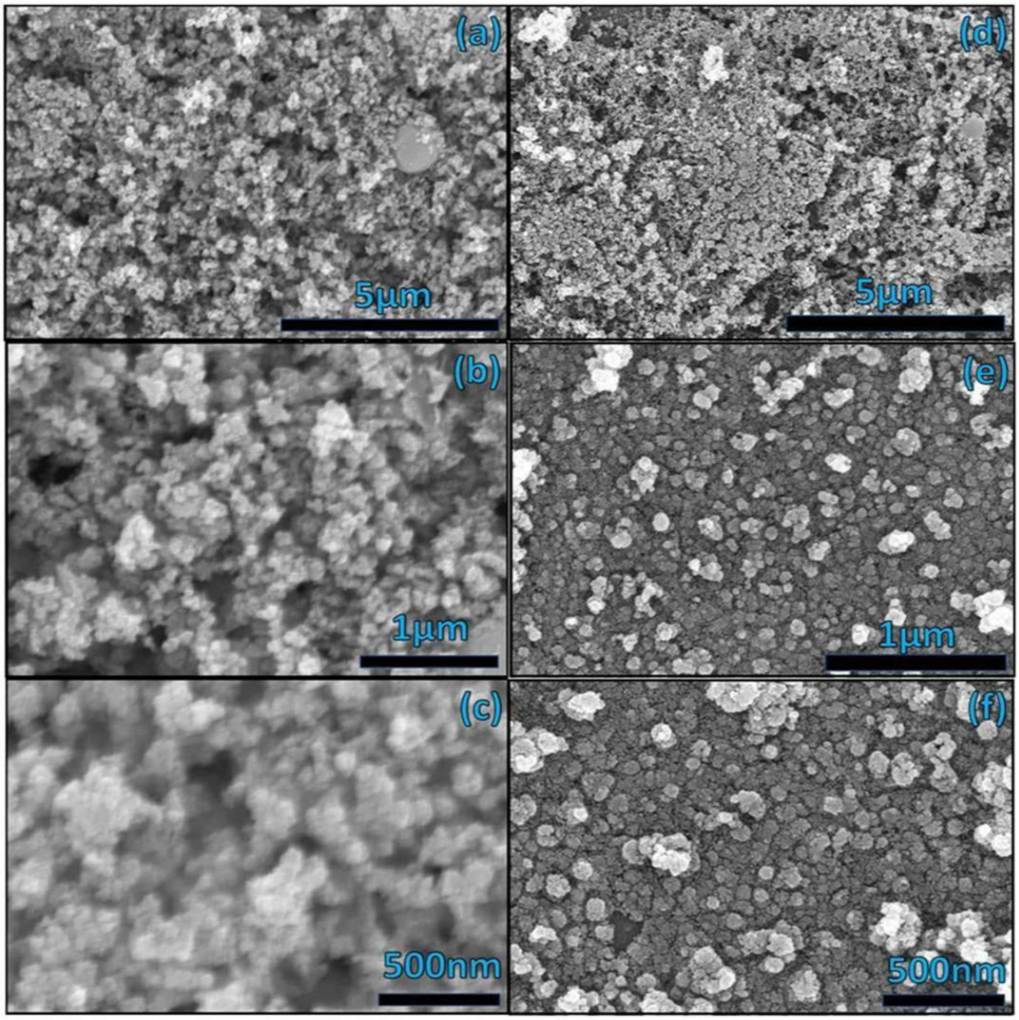

Fig. 2. FE-SEM images of as-grown (a–c) and sulfurized (d–f) CZTS thin films.

cuit current density (*Jsc*) of 5.5 mA/cm^2, fill factor (*FF*) of 0.54% and power conversion efficiency (η) of 2.08% of CZTS on FTO device. CdS quantum dots have created exciton which rapidly migrates to the interface and splits up into electron and hole [12]. This may be related to exciton and charge separations have enhanced efficiency nanostructure heterojunction solar cells. According to the literature

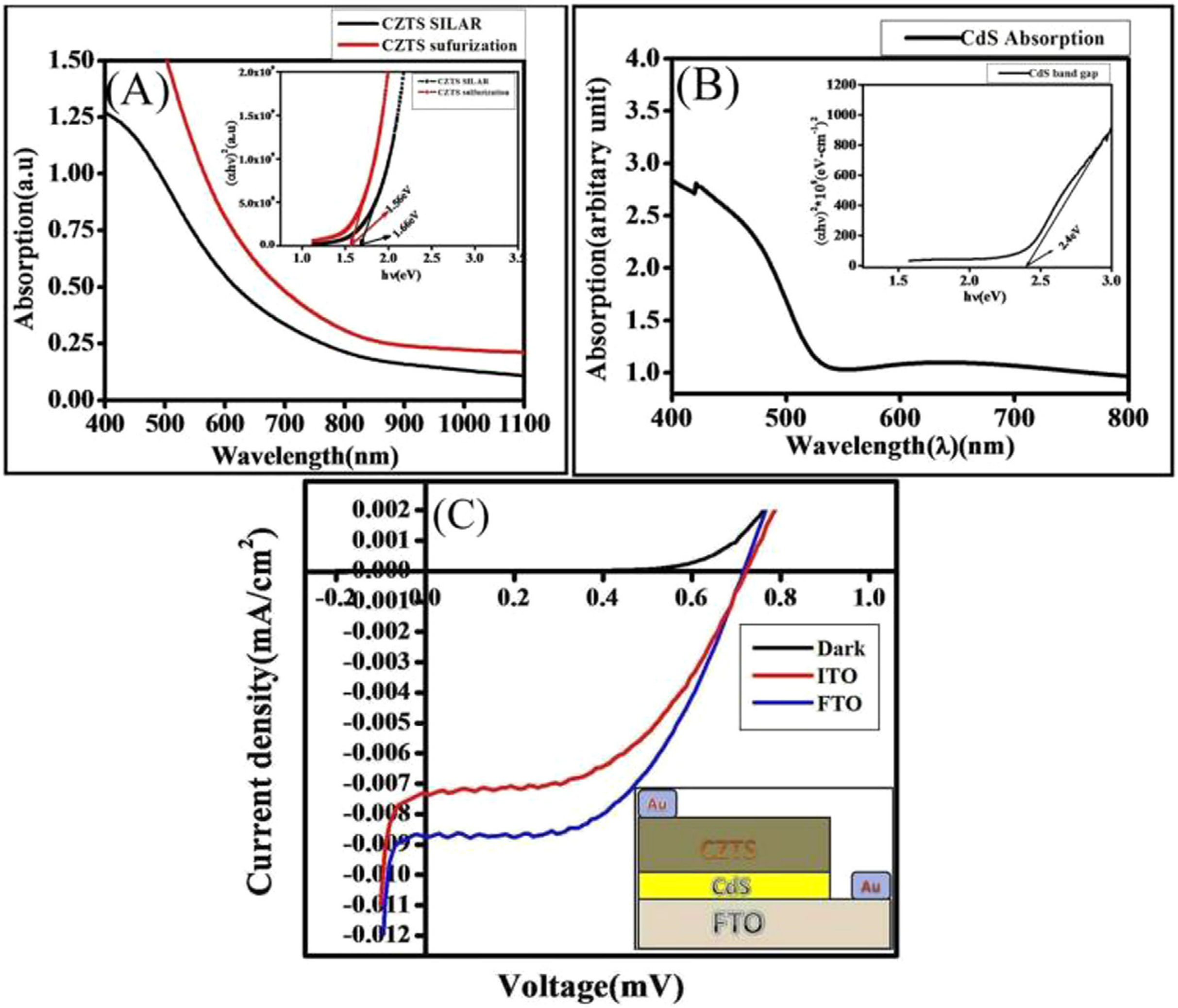

Fig. 3. (A) Optical absorption spectra of as-grown and sulfurized CZTS thin films and insert show the band gaps; (B) optical absorption spectrum of CdS thin film and insert show the band gap (C) J-V characteristic curves of CZTS thin films deposited on ITO and FTO substrates.

FTO conducting substrates have more compactness, uniform morphology and also good interface with CZTS materials but CZTS diffuses into the ITO substrate [21]. On the exposure of light, sample ITO shows 1.68% efficiency and sample FTO shows 2.08% efficiency.

4. Conclusions

CZTS thin films were successfully deposited by low cost SILAR method on a glass substrate at room temperature. It is found that as-grown CZTS films grown showed amorphous in nature but due to annealing under sulfur atmosphere transformed into kesterite structure with preferred orientations along (1 1 2) plane and average crystallite size was to be ~18 nm. CdS thin film average crystallite size confirmed that quantum dot and is to be ~8 nm. Leaf like morphology of CdS thin film confirmed by FE-SEM images. FE-SEM images of CZTS thin films show dense morphology with white pores but after annealing more uniform and compact morphology was observed. CZTS thin film on ITO substrate shows the power conversion efficiency 1.68% but CZTS thin film prepared on FTO substrate enhanced efficiency up to 2.08%. CZTS on ITO substrate annealed at high temperature gets diffused. The sulfurized CZTS films show excellent structural, optical and photovoltaic's properties. From above study, we can conclude that sulfurization makes a favorable impact on the CZTS thin film and FTO substrate enhanced the efficiency in higher temperature.

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