Nanocrystalline $Cuco_2se_4$ Thin Film Counter Electrode for Dye-Sensitized Solar Cells

A. Murugan, V. Siva, A. Shameem, S. Asath Bahadur

Abstract: ***Nanocrystalline $CuCo_2Se_4$ thin film have been deposited on over the micro slide by simplest route of successive ionic layer adsorption and reaction(SILAR) method. The $CuCo_2Se_4$ film was understand by Structural, morphological, and optical. The X-ray diffraction analyses confirm the formation of Cubic crystalline structure, than calculated grain size, dislocation density, and microstrain. The morphology of the film is homogeneous and agglomerated surface. The annealed $CuCo_2Se_4$ film are shows good optical absorption and the optical energy band gap energy is 1.90 eV, thus the suitable candidates for dye-Sensitized solar cell(DSSCs) application.***

Keywords: $CuCo_2Se_4$, SILAR, DSSCs, UV-Vis.

I. INTRODUCTION

Last few years energy demand due to increasing population. Limitations on the conventional energy sources, the focus on maximum consumption of the solar energy. Now days silicon based material are used to photovoltaic application, it have more expensive. Therefore need for economical materials if possible of direct optical energy band gap materials. DSSCs, is one of the most hopeful solar cells, DSSCs is overcome by silicon based solar cell such as ease to manufacture and low cost. DSSC is constructed with a counter electrode (CE), a redox-couple electrolyte, natural or organic based dyes and a working electrode, it made-up by sandwiched between the electrodes [1].

Platinum (Pt) free CE electrodes have been used in research laboratory due to its outstanding performance of chemical stability and electro catalytic activity. Unluckily, the high cost and low present ratio at earth and its produce a difficulty for large-scale application of DSSCs. Therefore improvement of low-priced CE materials with extraordinary electro catalytic activity and significance for real-world applications. The most of CE are used to carbon, conductive polymers, metal compounds, and graphene, like oxide, nitride, carbide, selenide and sulfide [2]-[8].

The metal selenides is a great attention due to their unique electronic properties, stimulating chemical behaviors, and wide multiplicity of application. Nanocrystalline $CuCo_2Se_4$ thin film have been deposited on to micro slide by SILAR method. SILAR is mostly unique because of homogenous deposition is possible on complex shape, its simplicity and deposited large area, economical cost and operating low temperature[9]. Annealed film was analysis by Structural, functional group, morphological, and optical properties. Ternary $CuCo_2Se_4$ film have good absorption in and the optical energy band gap is calculated by using tauc's plot and obtained band gap is 1.90 eV suitable candidates for solar cell application.

II. EXPRIMENTAL

A. Material and methods

The Nano-crystalline $CuCo_2Se_4$ thin film was deposited on to glass substrate by SILAR method. Copper chloride, cobalt chloride, and sodium selinite anhydrous were used as analytical grade regent and without any further purification for this film deposition. Double distilled (DD) water, ethanol were used as a solvent and washing of glass substrate.

The substrate is commercially available micro glass slide and the size of dimensions 25mm x 75mm x 1.5mm. The substrate activation process begin with etching the substrate, the substrate dipped in chromic acid for 3 minutes, then rinsed with double distilled water, and substrate dipped vertically in dilute HF for 2 minutes, then the substrate rinsed with DD water and finally substrate was ultrasonically cleaned under the DD water bath for 30 minutes.

The cation precursor solution was initially prepared by Cu^{2+} solution and Co^{2+} solution in separate beaker are stirrer for 30 minutes. Then the Cu solution is added drop wise in to Co solution under the stirring condition. After mixing the cation solution was stirred for an hour. The anion (Na_2SeO_3) solution was prepared by single bath which stirred in one hour. Both precursor solutions are prepared in 50 ml double distilled water. Both cation (pH=6) and anion (pH=7) precursor solution are maintained in stable pH at the end of the film deposition process.

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Precursor solution was taken 2:1:3 ratio of Cu, Co, and Se. The cationic and anionic precursor solution dissolved in 50 ml of double distilled water. Immersion of the cleaned substrate in cationic precursor solution for 30s ions was adsorbed on active center of the substrate surface. Then the substrate was rinsed in DD water for 20s to remove the loosely adsorbed cation from the surface of the substrate and to get the homogeneity. The substrate was subsequently dipped in the anionic solution for 30s. The sulfide ions reacted with adsorbed cations on the substrate surface. Finally substrate was rinsed in DD water for 20s to remove the unreacted cation, anion and powder particles from the substrate. Both rinsing water bath are maintained at 65 °C.

The above mention four steps for one SILAR cycle than similarly to 40 cycles were deposit by $CuCo_2Se_4$ thin film. After complete deposition, film was dried at 60 °C under the vacuum oven for one hour. The film was annealed at 300 °C for 2 h in muffle furnace at air atmosphere. In this SILAR method pH, temperature of the precursor solutions, concentration, and immersing period duration are significant parameter. The film was deposited on both side of the glass substrate.

B. Characterization

The $CuCo_2Se_4$ thin film structural was confirmed by powder X-ray diffraction (Bruker D8 advance ECO systems). The morphology and elemental confirmation can be investigated by scanning electron microscope (ZEISS EVO 18). The functional group analysis by Fourier transform infrared spectra (FT-IR) of the film were taken wavenumber from 4000–400 cm^{-1} (Shimadzu-IR Tracer-100). Optical absorption of the film were carried out in the wavelength range of 300–1100 nm using UV–Vis. spectrophotometer (Shimadzu-1800).

III. RESULT AND DISCUSSION

A. Structural analysis

Figure 1 shows the XRD patterns of the annealed $CuCo_2Se_4$ thin film. The XRD peaks reveal the crystalline nature of $CuCo_2Se_4$ with a cubic structure having (006) preferential orientation. The observed XRD peaks at 2θ value 31.89, correspond to (006) planes. The observations are in good agreement with the literature [10], [11]. The grain size (D) is calculated by scherrer formula [12]

$$D = \frac{0.9\,\lambda}{\beta COS\theta}$$

where, λ is the wavelength of the Cu Kα X-ray source, β is the full width at the half maximum, θ is the bragg's angle. The calculated grain size of the annealed CuCo2Se4 film is 57nm. The structural parameters of $CuCo_2Se_4$ film have been calculated by dislocation density and microstrain, evaluated from the equation.

$$\delta = \frac{1}{D^2}$$

$$\varepsilon = \frac{\beta cos\theta}{4}$$

The micro strain and dislocation density calculated values is 0.0029 $line^{-2}$ m^{-4} and 1.16788×10^{15} $lines/m^2$ respectively.

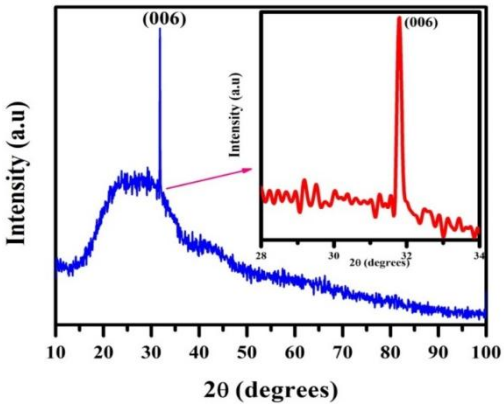

Fig. 1. Powder XRD pattern of $CuCo_2Se_3$ thin film

B. Fourier transform infrared spectra

FT-IR spectrum of $CuCo_2Se_4$ thin film taken in the range 4000–400 cm^{-1} shows in Figure 2. The functional groups of substrate surface bound molecules are identified by FTIR. Expected functional groups were present and metal selenium vibration at 669 cm^{-1} is assigned to the Co-Se vibration.

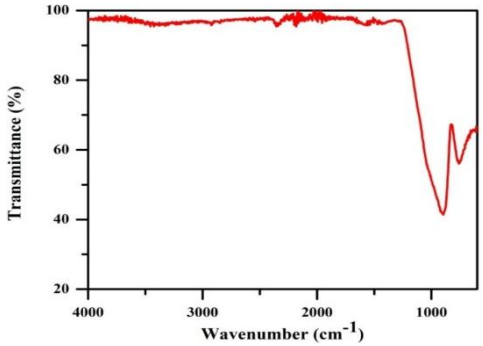

Fig. 2. FTIR spectrum of $CuCo_2Se_4$ thin film

C. Surface morphology analysis

The $CuCo_2Se_4$ film surface morphology of the annealed film has taken from SEM is show in Figure 3. From this micrograph, it is evident that the surface has well deposited agglomerated surface and without any visible cracks or holes which is suitable for solar cell application. The $CuCo_2Se_4$ film surface is covered partly by sphere-shaped micro-crystallites and the size of the sphere-shaped particle are roughly calculated nearby 200 nm.

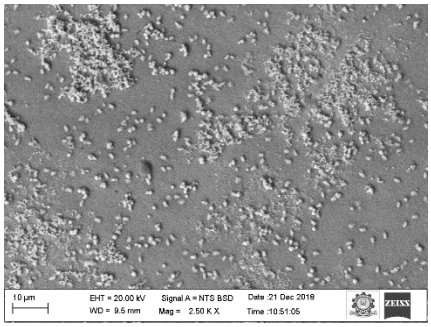

Fig. 3. SEM image of the $CuCo_2Se_4$ thin film

C. Optical properties

Figure 4 shows the UV-Vis absorbance spectra of $CuCo_2Se_4$ film. The deposited film shows good absorption in the visible regain, spectrum rang 400 to 800 nm confirm that is a good applicant for economic and environment friendly solar cell absorber layer and has suitable band gap for thin film solar cell. The band gap of the material formed in the deposits is calculated from the optical energy band gap using Tauc's plot [13].

$$\alpha = \frac{A(E - Eg)^n}{E}$$

From equation α is the absorption coefficient, E is the photon energy(eV), Eg is the optical energy band gap(eV). The superscript n, is a constant which given the values is 1/2, 3 and 3/2 for direct, indirect and indirect forbidden allowed respectively. Figure 5 show in the Tauc's plots for the annealed CuCo2Se4 film. The optical energy band gap of the CuCo2Se4 film is calculated as1.90 eV, which is required for any solar cell material.

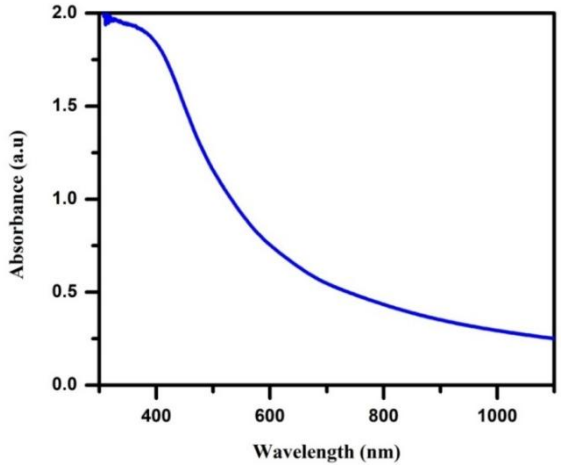

Fig. 4. UV-Vis absorbance spectrum of $CuCo_2Se_4$ thin film

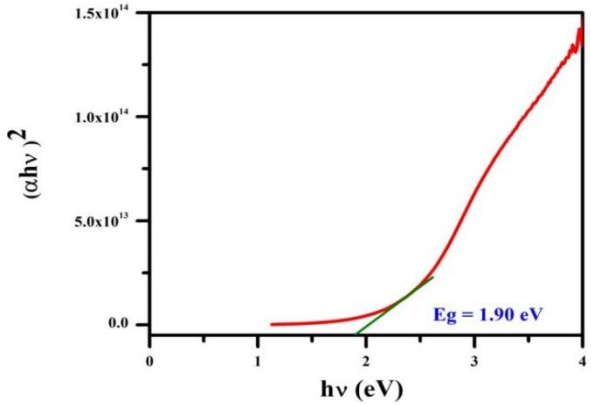

Fig. 5. Tauc's plot

IV. CONCLUSION

The $CuCo_2Se_4$ thin film have been deposited over on micro glass substrate by SILAR method. Powder XRD shows good crystalline nature and grain size of the $CuCo_2Se_4$ thin film evaluate by Scherrer's equation as 57 nm. The morphology of annealed film shows spherical particle on the substrate and well uniformly deposited without any crack. Optical property of the film shows good absorbance in visible wavelength it is suitable for solar cell absorber material because the optical energy band gap is 1.90 eV. Therefore, the $CuCo_2Se_4$ system may be an attractive choice for counter electrode in DSSCs.

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