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Novel synthesis of Cu_2CoSnS_4 thin films for photovoltaic application

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ABSTRACT

Chemical spray pyrolysis technique (CSPT) can be used for preparation of thin films that can be utilized in different fields such as solar cells, sensors, and solid oxide fuel cells. In spray pyrolysis the deposition rate, area and thickness of the thin films can be controlled at a wide working temperature range such as, from 100 °C to 500 °C for soda lime glass (SLG) substrates. The present paper reports synthesis and characterizations of the spray deposited CCTS films at substrate temperature of 350 °C. A power conversion efficiency of 1.78 % is observed for the photoelectrochemical solar cell fabricated with CCTS film on FTO substrate as working electrode, Sodium sulphate as electrolyte and platinum based counter electrode.

Keywords: Cu_2CoSnS_4thin films; spray pyrolysis; Photoelectrochemical

INTRODUCTION

Thin films are useful in variety of applications such as solar cells, sensors, and solid oxide fuel cells [1]. Most of the chemical synthesis processes for preparation of thin films like; hydrothermal, sol-gel, solid state reaction and liquid phase synthesis require a long heat treatment processes. Additionally, these methods need precise control over preparative parameters like pH, temperature, controlled supply of reacting species, and use of stabilizing agent to preserve monodispersity, followed by post processing steps like washing, drying, and calcination [2–5]. These post deposition processes are time consuming that increase production cost. To reduce high mfg cost of large scale production of thin films which are used in various applications it is essential to implement single step process which is more suitable and economic. Among the diverse methods accessible for deposition of thin films, the chemical spray pyrolysis technique (CSPT) is widely used and has many advantages such as non-vacuum, easy handling and large deposition area [6]. CSPT can facilitate working temperature range from 100 °C to at least 500 °C which is quite useful for SLG substrates, those can be preheated using temperature control arrangement.

The present paper reports synthesis and characterization of Cu_2CoSnS_4 (CCTS) thin films prepared by CSPT for photovoltaic application. CCTS is a compound semiconductor, which has stannite structure and crystallizes in tetragonal unit cell, inside which all three metals are tetrahedrally surrounded by sulfur atom, and each sulfur atom is surrounded by one Co, one Sn, and two Cu atoms [7] . The p type conductivity and direct band gap values in the range of 1.46 eV to 1.61 eV of CCTS are of significant importance as an absorber layer in development of efficient thin films solar cells (TFSC). Due to its direct band gap CCTS reduces the material need in comparison with other indirect band gap materials like silicon [8]. The availability of copper, cobalt, tin, and sulfur in earth's crust is found to be 50 ppm, 20 ppm, 2.2 ppm, and 260 ppm respectively. To reduce the pressure on current photovoltaic (PV) technology much attention is required on the development of PV technology rooted in abundant and nontoxic elements like CCTS [9].

To carry out deposition of thin films by CSPT, here electronic control system is designed with the help of single push button switch and potentiometer. Control system also handles automatic movement of nozzle through a slider crank arrangement driven by dc geared motor. Solid state relay is used to make ON/OFF arrangement of heater to keep the temperature in the desired range. The system is designed around open source Arduino microcontroller platform with 0 °C to 1000 °C range k-type thermocouple, and MAX6675 to sense temperature of heater plate in closed loop arrangement. The working temperature range is selected in the range of (± 2) °C with respect to threshold set point entered by user through PID temperature controller.

METHODOLOGY

The reaction chamber of spray pyrolysis unit used for preparation of thin films has dimensions of $90\,cm\,(length)\times 60\,cm\,(breadth)\times 90\,cm\,(height)$ is a metallic chamber. The inner sides of a metallic chamber are covered by fire proof cement board to sustain the temperature of reaction chamber due to heat loss. The different by-products evolved during the pyrolysis are removed by exhaust fan fitted to reaction chamber. The electric plate heater was made from 1500 W nichrome coil, which is wound parallel with a spacing of 1 cm on a ceramic base having thickness of 2.5 cm and diameter of 19 cm. The free ends of coil are connected to 230V/16A power supply through solid state relay. The Arduino platform activates and deactivates the relay as per requirement of temperature to accomplish the deposition of thin films. The preheated SLG substrates with dimensions $7.5\,cm\,(length)\times 2.5\,cm\,(breadth)\times 1.4\,cm\,(thickness)$ are used for deposition of Cu_2CoSnS_4 thin films. These substrates are kept on circular stainless steel plate which has a diameter of 20 cm and thickness of 0.5 cm. The atomization of the precursor solution is achieved by filtered compressed air. Pressure of the compressed air is kept at ≈1 bar. Single phase, 1 HP compressor provides compressed air which is used as a carrier gas.

A specially designed borosilicate glass nozzle is used for atomization of precursor solution by carrier gas. Pressure of the carrier gas creates a vacuum at the tip of nozzle, due to which precursor solution is sucked at a liquid opening. It initiates the spraying of precursor solution [10]. To achieve the regular deposition of the thin films, mechanized to and fro movement with frequency of 0.16 Hz has been employed to spray nozzle. For deposition of CCTS thin film, the precursors used were $CuCl_2.2H_2O$ (Cupric Chloride) for copper, $CoCl_2.6H_2O$ (Cobalt Chloride hexahydrate) for cobalt, $SnCl_4.5H_2O$ (Stannic Chloride) for tin and CH_4N_2S (thiourea) for sulfur. The 0.05M $CuCl_2.2H_2O$, 0.025M $CoCl_2.6H_2O$, 0.025M $SnCl_4.5H_2O$ solutions were prepared separately in methanol as a solvent. The appropriate amount of thiourea powder was dissolved in methanol so that the ratio of cations to anions should be more than stoichiometry in the final precursor solution. The molarity of thiourea was chosen in excess than the stoichiometry to avoid the loss of sulfur at elevated temperature [11]. All the cationic solutions were mixed together in a proper order, which resulted into brown colored solution with pH≈ 1. Thiourea was added drop wise to this cationic solution under vigorous stirring. The addition of complete thiourea to this cationic solution resulted into change in the pH value of the final precursor solution to ≈ 3, and has dark blue color. With a flow rate of 5 mL/min, the 80 mL of the precursor solution was sprayed onto SLG and FTO substrates which were preheated using temperature control arrangement. Fig.1 shows the schematic of spray pyrolysis unit used for deposiion of CCTS thin films.

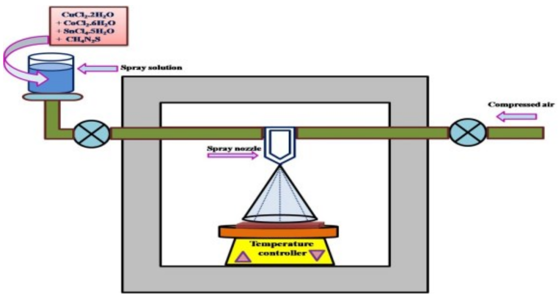

Fig.1-Schematic of spray pyrolysis unit used for deposition of CCTS thin films

The structural properties of spray deposited CCTS thin films were studied by using X-ray diffractometer (XRD) operated at 40 kV, 30 mA with Cu K_{α}radiation (λ=1.5406 Å). Surface profiler (Ambios, XP-I stylus profiler, USA) was used to carry out the thickness measurement of the CCTS thin films. The surface morphology of the CCTS films was studied with a MIRA 3 FE-SEM microscope (TESCAN) attached with EDX detector (Oxford Instruments, UK). UV-Visible spectrophotometer (UV 1800, Shimadzu, Japan) was used to record UV-visible absorbance spectra of the CCTS thin films.

RESULTS AND DISCUSSION

The reflections corresponding to (112), (204) and (312) planes are observed at diffraction angles 28.64°,47.36°and 56.38° respectively. The spray deposited CCTS thin film is polycrystalline in nature and show a preferred orientation along (112) plane. From XRD spectrum it is confirmed that the spray deposited CCTS thin film exhibit stannite structure compared to standard JCPDS card no. 00-026-0513. The average crystallite size (D) is calculated by Scherrer`s equation [12].

3.1 Structural analysis:

Fig.2 shows XRD pattern of CCTS thin film deposited at a substrate temperature of 350 °C.

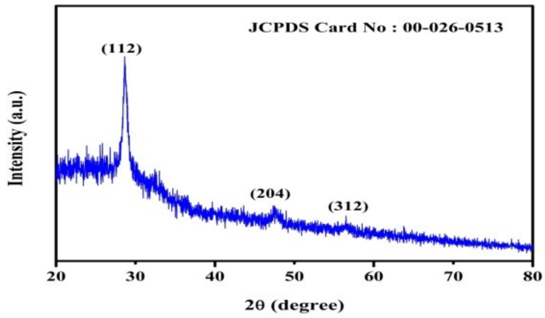

Fig.2 -XRD pattern of CCTS thin film deposited at a substrate temperature of 350 °C

$$D = \frac{k\lambda}{\beta\cos(\theta)} \qquad (2)$$

Where k is the shape factor, usually taken as 0.9 for spherical crystallites, λ is the wavelength of X-ray used, β is the FWHM and θ is the Bragg's angle. The average crystallite size calculated for the CCTS films deposited at 350 °C is equal to 11.78 nm. Table 1 shows the structural parameters obtained for CCTS thin films.

3.2 Morphology of the films:

Fig.3 shows the FE-SEM image of the CCTS film deposited at a substrate temperature of 350 °C.Flake like morphology is observed for the CCTS thin film deposited at substrate temperature of 350 °C. Surface of the film shows the chain of flakes at some region with nonuniform distribution of flakes. The density of the flakes is not the same all over surface. The surface morphology of the films seems to be compact with existence of few of voids over the film surface.

3.3 Thickness measurement:

The thickness of the CCTS film deposited at a substrate temperature of 350 °C is found to be 325 nm.

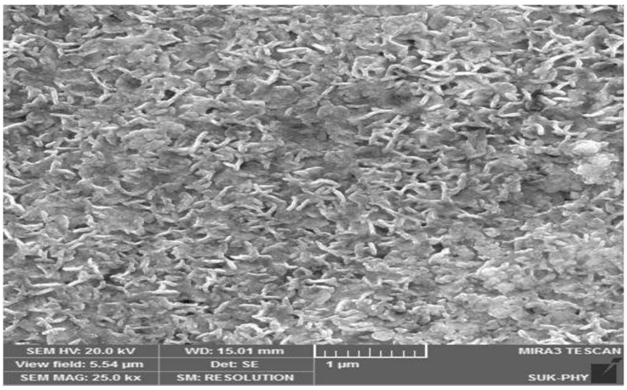

Fig.3-FE-SEM image of CCTS film deposited at 350 °C with 25k× magnification.

3.4 Compositional analysis:

The elemental composition of different constituent elements in the CCTS film is analysed using EDAX. The EDAX spectra of the films deposited at a substrate temperature 350 °C is shown in Fig.4.

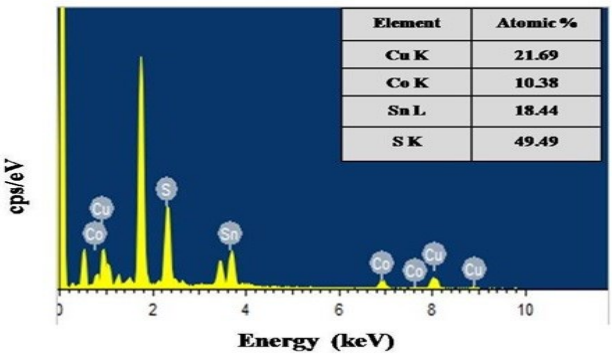

Fig.4- EDAX spectrum of CCTS film deposited at 350 °C

3.5 CCTS formation mechanism

Thin film Material	Substrate temperature (°C)	Miller indices (hkl)	Standard diffraction angle (2θ)°	Observed diffraction angle (2θ)°	Calculated d(Å)	FWHM (rad)	Crystallite size D (nm)	Average Crystallite size (nm)
CCTS	350°C	(112)	28.59	28.64	3.11	0.010	13.84	11.78
		(204)	47.56	47.36	1.91	0.013	11.31	
		(312)	56.47	56.38	1.63	0.015	10.21	

The chemical reaction for CCTS formation on SLG substrates is given by

$$2CuCl_2 + CoCl_2 + SnCl_4 + 4SC(NH_2)_2 + 13H_2O \xrightarrow[\Delta]{\text{Thermal decomposition } (CH_3OH)} Cu_2CoSnS_4 + 8NH_4Cl\uparrow + 4CO_2\uparrow + 5H_2O\uparrow + Cl_2\uparrow \quad (1)$$

The peaks corresponding to different constituent elements like Cu, Co, Sn, and S are clearly seen in the EDAX spectrum of the films. For the films deposited at 350 °C the composition ratio of Cu: Co: Sn: S is found to be 2.08:1:1.77:4.76 the composition of the films appears slightly Sn, and S rich. The S as to mental ratio is found to be 0.97.

3.6 Optical properties of CCTS thin film:

The relation between absorption coefficient α and incident photon energy hν is given by equation [13].

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (3)$$

where A is proportionality constant, $E_g$is optical band gap energy, n is an index representing the optical absorption process and it takes values equal to 1/2 or 2 for the direct and indirect allowed transitions respectively. The optical band gap of CCTS thin film can be obtained by extrapolating the linear portion of the plots $(\alpha h\nu)^2$ against hν at α = 0 as shown in Fig.5

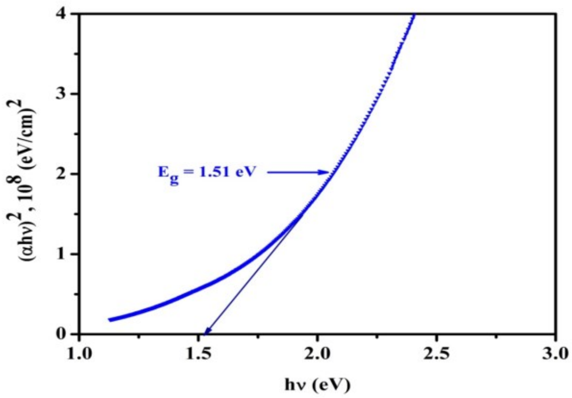

Fig.5- Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CCTS film deposited at substrate temperature 350 °C

Table 2-Parameters of PEC solar cell based on CCTS thin film as working electrode deposited at substrate temperature of 350 °C

Substrate Temperature (°C)	J_{sc}(μA/cm²)	V_{oc} (mV)	J_{max} (μA/cm²)	V_{max} (mV)	FF	Efficiency (η)%
350 °C	12.73	350	8.07	134	0.24	1.78

The straight line nature of graph indicates the direct allowed transitions. Thus the index n takes value equal to ½. The energy band gap value of the CCTS films deposited at substrate temperature 350 ˚C is found to be 1.51eV. The obtained band gap value for CCTS films is quite close to the most promising band gap value of the materials used for a solar cell application [14].

3.7 Photoelctrochemical cell performance (PEC) study:

The PEC solar cell is fabricated with two electrode configuration in which CCTS thin film deposited on FTO substrate was used as working electrode, and platinum based counter electrode with spacing of 1 cm between working electrode and counter electrode. The electrolyte used was 0.5 M Na_2SO_4, pH of which was adjusted to ≈ 10 by adding few drops of 0.5 M NaOH. A 500 W tungsten lamp with intensity of 60 mW/cm² is utilized as light source of illumination for PEC measurement. The light is exposed on active area of 0.25 cm² of working electrode, by masking rest of its area with insulating tape. Fig.6 shows the current density-voltage (J-V) characteristics of the CCTS based photoelctrochemical solar cell, under illumination.

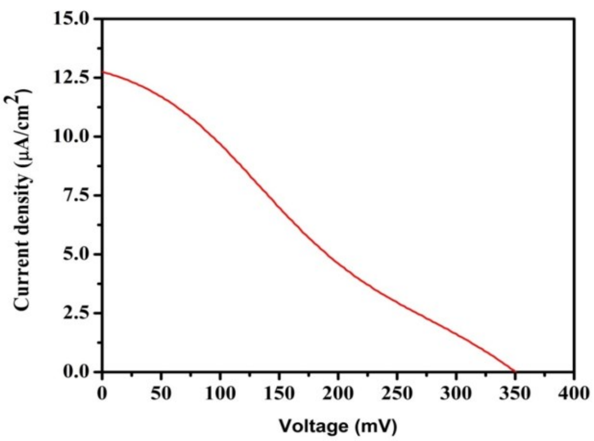

Fig.6- Current density-voltage (J-V) characteristics of the CCTS based photoelctrochemical solar cell

The fill factor (FF) and power conversion efficiency (η) of the PEC solar cells is calculated by using equations

$$FF = \frac{J_{\max} \times V_{\max}}{J_{sc} \times V_{oc}} \quad (4)$$

$$\eta = \frac{J_{sc} \times V_{oc}}{P_{in}} \times FF \times 100 \quad (5)$$

Where V_{oc} is the open circuit voltage, J_{sc} is the short circuit current density, V_{max} is maximum voltage, J_{max} is maximum current density, FF is fill factor, and P_{in} is input power density of illuminated light. Table 2 summarizes the results for PEC performance of CCTS thin film deposited at substrate temperature of 350 ˚C. The power conversion efficiency of 1.78 % is obtained for the PEC cell fabricated with CCTS film as working electrode that may be ascribed to optimal band gap value of the CCTS film, which helps to enhance effective absorption of incident light, while compact morphology of the film promotes fast electron transfer in the PEC cell fabricated with CCTS as working electrode [15].

CONCLUSION

The stannite structure of CCTS thin films with preferential orientation along (112) plane was confirmed by XRD study. The presence of constituent elements like Cu, Co, Sn and S is confirmed from EDAX spectrum of CCTS thin films. Photoelectrochemical solar cell based on CCTS thin film as a working electrode provided a conversion efficiency of 1.78 %. This novel synthesis of CCTS thin films for photovoltaic application will open a new avenue for development cost effective thin film solar cells rooted in earth abundant and nontoxic elements.

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