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Photoelectrochemical properties of In_2Se_3 thin films: Effect of substrate temperature

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ABSTRACT

In_2Se_3 thin films have been deposited onto fluorine doped tin oxide coated (FTO) glass substrates at various substrate temperatures by spray pyrolysis. The photoelectrochemical cell configurations were In_2Se_3 thin film/1 M (NaOH + Na_2S + S)/C. From capacitance–voltage (*C–V*) and current–voltage (*I–V*) characteristics; it is concluded that In_2Se_3 thin films are of n-type. The Fill factor (FF) and solar conversion efficiency (η) were calculated from photovoltaic power output characteristics. In this instance, the highest measured photocurrent density of 1.05 mA/cm^2 and open circuit voltage of 261 mV is observed for film deposited at 350 °C resulting in maximum power conversion efficiency (η) and fill factor (FF) to be 0.71% and 0.51% respectively. Electrochemical impedance spectroscopy study shows that the In_2Se_3 film deposited at 350 °C shows better performance in photoelectrochemical cell. The performance of indium selenide thin film observed in our work can motivate further studies concerning solar energy conversion.

1. Introduction

World energy demand is continually increasing inexorably in the last ten decades connected with population growth and infinite industrial development. Renewable solar energy is expected to be the fastest growing and a potential solution to the energy sustainability. The rapid decrease in cost of photovoltaic modules and systems in the last few years has opened new perspectives for using solar energy as a major source of electricity in the coming years and decades [1]. Photoelectrochemical (PEC) process is one of the promising approaches to convert solar energy into chemical as well as electrical energy [2–6].

PEC measurement is based on charge transfer between the electrolyte, semiconductor and electrode when irradiated with photons. In general, the charge separation and transfer mechanism are the key issues affecting the PEC cell performance. The research interests on the phenomena of charge transfer across a semiconductor–liquid interface shows dramatic growth due to the increasing requirements of solar energy converting applications [7]. The basic requirements for good thin film photoelectrode for PEC cells are low resistivity and larger grain size. Large grain size leads to reduction of the grain boundary area of the thin film leading to an efficient energy conversion. The low resistivity of the photoelectrode is required to minimize the series resistance of the PEC cell which leads in increasing the short circuit current [8–9].

Currently, the investigations on PEC cells, mainly focus on the semiconductor materials with wide band gaps, such as TiO_2 [10,11] and ZnO [12,13], which respond only to ultraviolet light (accounting only 4% in solar spectrum). With aim of utilizing the solar energy more effectively, intensive efforts have been carried out to investigate the visible light (accounting 43% in solar spectrum) responsive semiconductors ($\lambda > 400$ nm) [14].

Indium selenide (In_2Se_3) is an effective visible light-driven semiconductor material with hexagonal crystal structure, showing direct band gap of about 1.62 eV [15]. Indium selenide is an n-type semiconductor belonging to III–VI family, which has been widely studied, due to its potential application as an absorber layer in photovoltaic devices. This is because of its high absorption coefficient and optimum energy band gap which are suitable for solar to electrical/chemical energy conversion. In_2Se_3 exhibits at least three different crystalline modifications denoted as α, β and γ with transition temperatures of 200 and 650 °C, respectively for $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transition [16,17]. Indium chalcogenide thin films can be prepared by using various deposition techniques like chemical bath deposition [18,19], sputtering [20–22], solvothermal method [23], MOCVD [24] electrochemical technique [25], electrodeposition [26,27], spray pyrolysis technique [28,29], etc.

Yan et al. [20–22] have deposited In_2Se_3 films by magnetron radio-frequency (RF) sputtering technique and subsequently

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analyzed these films by various characterization techniques. Their analysis showed that γ-In_2Se_3 nanostructures can be successfully grown via magnetron sputtering process with a direct band gap 1.94 eV. However, their analysis indicated that film properties strongly depend on the process parameters and there is possibility of using In_2Se_3 thin film in various next-generation photoelectric and optical-memory device applications. Looking forward to Yong Yan et al.'s study, we got motivation and hence tried to study photoelectrochemical properties of In_2Se_3 thin films deposited by using a different technique (spray pyrolysis), since the study of photoelectrochemical analysis plays an important role in device fabrication. Keeping in view all these aspects the present study deals with a photoelectrochemical investigation of indium selenide thin films deposited by computerized spray pyrolysis technique. The results obtained are discussed and compared with literature wherever possible.

2. Experimental details

2.1. Deposition In_2Se_3 thin films

Indium selenide thin films are deposited onto FTO coated glass substrates (sheet resistance 7–8 Ω/□) by a computerized spray pyrolysis method (discussed elsewhere [30]) with substrate temperature of 300–400 °C at the interval of 25 °C. Equimolar (0.05 M) aqueous solutions of indium chloride ($InCl_3$) and selenourea ($H_2NC(Se)NH_2$) were used as starting materials in the ratio 2:3. The substrate temperature was controlled by an iron-constantan thermocouple. A spray rate of 3–4 ml/min was kept constant throughout the experiment. The distance between the substrate and the nozzle was 28 cm. The air was used as carrier gas. After deposition, the films were allowed to cool at room temperature.

2.2. Fabrication of PEC solar cell

The as deposited indium selenide thin films were used to prepare a PEC cell with a standard three electrode configuration, with n-indium selenide thin film as active photoelectrode (area 1 cm^2), graphite as a counter electrode and Saturated Calomel Electrode (SCE) as a reference electrode. The redox electrolyte used was 1 M polysulphide (NaOH + Na_2S + S). A 100 W tungsten filament lamp (intensity 20 mW/cm^2) was used as a source of light. A gap of 0.2 cm was kept between the photoelectrode and counter electrode. Power output characteristics were measured by using, a two electrode configuration. LCR (Aplab model 4912) at built in frequency 1 kHz was used to plot Mott–Schottky curves. Electrochemical impedance spectroscopy properties were studied using CHI 604D electrochemical workstation (CH Instrument Company, USA). Three-electrode system was used for EIS studies in which indium selenide thin films on FTO-coated substrate were used as a working electrode, platinum mesh as a counter electrode and SCE as a reference electrode. The frequency range examined was 1 MHz to 10 mHz.

3. Results and discussion

The crystal structure of indium selenide thin films was studied by using X-ray diffraction technique with Cu Kα radiation (1.5406 Å). X-ray diffraction patterns revealed the films of indium selenide are polycrystalline with hexagonal crystal structure irrespective of substrate temperature. It was observed that the high intensity reflection peaks at $2\theta = 25.66°$ (100) plane, $2\theta = 27.26°$ (101) plane, $2\theta = 31.70°$ (102) plane and $2\theta = 45.34°$ (110) plane for In_2Se_3 thin film which indicates that the growth of the thin films occurred preferentially in the direction perpendicular to the sample's surface. A comparison of observed and the standard'd' values for (hkl) planes ensures that indium selenide shows hexagonal crystal structure irrespective of substrate temperature [31]. No peaks correspond to oxide phases, which demonstrates that the [Se]/[In] ratio we employed in spray deposition avoided the formation of undesirable oxide phases. This finding is supported by the absence of any oxide-related diffraction peaks when the solution was sprayed onto the glass substrate at the same temperature. The intensity of main peak (102) produced by In_2Se_3 thin film increased with the substrate temperature up to 350 °C, but it decreased slightly after 350 °C. Therefore, the film deposited at 350 °C had the highest intensity and it exhibited better crystallization than the other films deposited at other substrate temperatures. Initially, there were many crystallites present in the as-deposited films that exhibited less intense peaks and when the layers were deposited at a particular substrate temperature (350 °C) the small crystallites grew into larger ones with an improved crystallinity. The observed structural changes were attributed to the coalescence induced grain growth during the high temperature deposition process where smaller nuclei could easily rotate compared to the larger nuclei in order to minimize the interfacial energy [32]. After refinement, the cell constants were calculated to be $a = b = 4.014$ Å and $c = 9.64$ Å; which are consistent with the reported data [33]. The crystallite size for indium selenide thin films is found to be in the range of 18–26 nm.

The surface morphology of indium selenide thin films was investigated using SEM technique. Which show that all of samples were free of pinholes and cracks. The films were well coated, compact, and homogeneous, thereby making them suitable for photovoltaic applications. It is found that bandgap energy E_g decreases with increase in substrate temperature reaches a minimum value of 1.78 eV at 350 °C and further increases with increase in substrate temperature. The values of crystallite size and bandgap energy E_g for indium selenide thin films are given in Table 1. The room temperature electrical conductivities of the indium selenide thin films are in the range between 1.90×10^{-4} and 1.00×10^{-4} $(\Omega\text{-cm})^{-1}$. The polarity of thermo-emf was positive toward hot end with respect to cold end, confirming that In_2Se_3 thin films are of n-type.

3.1. Type of conductivity

PEC cells with configuration indium selenide/(1 M NaOH + 1 M Na_2S + 1 MS)/graphite were formed to check the type of conductivity exhibited by indium selenide thin films. In dark, PEC cell gives some voltage and current with negative polarity toward the indium selenide electrode. The origin of this voltage could be attributed to the difference between two half cell potentials in the PEC cell. When above junction is illuminated both short circuit current (I_{sc}) and open circuit voltage (V_{oc}) were increased with negative polarity toward indium selenide electrode showing that the films are of n-type [34,35].

3.2. Capacitance–voltage characteristics

The capacitance–voltage measurements provide useful information regarding the flat band potential and type of conductivity. In our case n-In_2Se_3/polysulphide interfaces were fabricated and the Schottky barrier capacitances were measured at a 1 Vpp–1 kHz as a function of the applied d.c. bias from −400 to 800 mV (versus SCE). Fig. 1 shows the Mott–Schottky (M–S) curves for n-In_2Se_3/polysulphide/C electrolyte system in dark for In_2Se_3 thin film deposited at various substrate temperatures. The nature of plot indicates typical n-type behavior. The non-linear nature of the graph is an indication of graded junction formation between

Table 1
Values of thickness, crystallite size and important PEC parameters for In_2Se_3 PEC cells.

T_s (°C)	t (nm)	D (nm)	E_g (eV)	V_{fb} (−V)	n_d	n_L
300	523	18	1.95	0.58	2.87	1.85
325	578	21	1.83	0.67	2.78	1.83
350	650	26	1.78	0.72	2.64	1.79
375	617	24	1.86	0.63	2.69	1.82
400	568	22	1.98	0.53	2.75	1.88

T_s; substrate temperature, t; thickness, D; crystallite size, E_g; bandgap energy, V_{fb}; flat band potential, n_d; ideality factor in dark, n_L; ideality factor under illumination.