Chapter 2

CHAPTER 2

EXPERIMENTAL: SYNTHESIS METHOD AND CHARACTERIZATION TECHNIQUES

This chapter describes the experimental methods and analytical details of synthesis of nanoparticles and thin film fabrication of solar cell devices.

2.1 INTRODUCTION

Recently, great attention is drawn towards the synthesis of nanoparticles, which are used in various applications. Several experimental techniques were used to synthesize and characterize the semiconducting nanoparticles. The synthesis of nanoparticles with required properties is a challenging task. Hence, the synthesis process plays an important tool for the development of nanostructures and nanoparticles with required properties such as crystallite size, surface area, pore size distribution, morphology etc., in order to meet the requirements for specific applications. The synthesized materials need to be characterized using different techniques to find out their structural and electrical properties. A description of the different synthesis methods and characterization techniques used in my work are presented in the following sections.

2.2 EXPERIMENTAL: METHODS OF NANOPARTICLES SYNTHESIS AND THIN FILM FABRICATION

The different methods that can be employed for the synthesis of nanoparticles are as follows,

- Ball-milling [1]
- Sol-gel [2]
- Solvothermal [3]
- Microwave [4]
- Hydrothermal [5]
- Co- precipitation [6]

Various synthesis process used for the thin film fabrication

Thin film deposition is broadly classified into two major categories; vacuum based physical deposition and non-vacuum based chemical deposition. Wide varieties of deposition techniques are available in the thin film photovoltaic field. Suitable synthesis methods can be used to prepare $Cu_2Ni_xSn_{(1-x)}S_4$ (CNTS) and $Cu_2Fe_xSn_{(1-x)}S_4$ (CFTS) nanoparticles with potential for use as ideal photovoltaic candidates. Generally non vacuum atmosphere ink based process are preferred because they are convenient, low cost and scalable.

The Vacuum deposition processes include, Sputtering [7] and Pulsed laser deposition [8] and the Non vacuum deposition processes include Electro deposition [9], Spray pyrolysis [10], Chemical vapor deposition [11], Chemical bath deposition [12] and Spin coating [13].

Among the available various experimental techniques, in the present study, chemical precipitation and hydrothermal methods have been used for the synthesis of $Cu_2Ni_xSn_{(1-x)}S_4$ (CNTS) and $Cu_2Fe_xSn_{(1-x)}S_4$ (CFTS) nanoparticles. Thin film fabrication, chemical bath deposition and spin coating method are used for window and buffer layers, which are briefly described in the following section.

2.2.1 Chemical precipitation method

The precipitation of multi-compounds system is termed as co-precipitation. To obtain the precipitation with well-defined stoichiometry of metal ions, the precipitation agent should satisfy the following conditions. In this method a salt precursor, commonly nitrate, chloride or oxychloride is dissolved in aqueous solution and then the corresponding hydroxide is precipitated by the addition of a base such as sodium hydroxide or ammonium hydroxide.

Among many physical and chemical methods, chemical co-precipitation method is more advantageous in preparing nanoparticles due to inexpensive apparatus, low power consumption, non-toxic byproducts, high homogeneity, high flexibility, effective size control and absence of need of vacuum. This technique is more suitable and economical for large scale production. In the present study, we have focused our attention on the effect of pH on the structural and optical properties of the synthesized nanoparticles [6].

2.2.2 Hydrothermal method

From the environmental perspective, hydrothermal methods are more environmentally benign than many other methods. Hydrothermal synthesis is typically carried out in a pressurized vessel called an autoclave with the reaction taking place in an aqueous solution. The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapor saturation. Hydrothermal synthesis is widely used for the preparation of metal oxide nanoparticles which employs the hydrothermal treatment for the precipitation of a metal precursor with water. In hydrothermal method the grain size, particle morphology, crystalline phase and surface can be controlled through regulation of the solution composition, reaction temperature, pressure, solvent properties, additives and aging time.

If the reaction temperature is 100 °C and above, the required pressure is developed in the vessel which encourages the nucleation and growth of the nanoparticles. At the same time, other experimental factors like quantity of solvents and precursors are also important to obtained fine nanoparticles. The hydrothermal method has several advantages like simple methodology, low processing temperature, low cost, high product purity and ability to control the particle size [14].

A major advantage of hydrothermal synthesis is that high temperature calcinations are not needed for the formation of oxides. A successfully synthesis of materials by this method depends on the selection of its precursors. It should possess appropriated process condition variables such as temperature, pH and reagent concentrations.

2.2.3 Chemical bath deposition method (CBD)

This is one of the easiest, cost-effective and scalable solution process techniques. Thin films grown by this technique are very uniform, adhesive, stable and hard. The growth of the thin film strongly depends on growth parameters such as, molarity of precursors, deposition temperature, stirring rate and pH of the precursor solution. Researcher have reported two types of nucleation during the deposition viz., homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation leads to the rapid formation of precipitation inside the bath and to have a control over this is one of the challenging while heterogeneous nucleation occurs at the substrate surface and particles grow gradually which leads to the formation of very uniform thin film. This CBD technique is based on controlled chemical reaction in solution which leads to the formation of the films. Most of the researchers have used this technique extensively to deposit CdS thin film which acts as a buffer layer in solar cell applications [15].

2.2.4 Spin coating

Spin coating is a method used to prepare uniform thin films on flat substrates. One drop of the prepared solution is placed on a well cleaned glass substrate, which is rotated at a high speed. As the substrate rotates the fluids spreads due to the centrifugal force. A programmable machine used for spin coating is called a spin coater. The substrate is rotated continuously, so that the fluid spreads and a thin film is formed on the substrate. The applied solvent is usually volatile and evaporates simultaneously. The thickness of the film also depends on the concentration of the solution. Spin coating is widely used in micro fabrication, where it can be used to create thin films with thickness around 100 nm. In order to get thicker film multi coating is done.

2.2.5 Substrate cleaning

The most important consideration in thin film deposition processing, is that the thin film should be adherent to the substrate. Poor adhesion is often caused by the dirt or impurities present on the substrate surface. These can be eliminated by cleaning the substrate prior to deposition as the quality of the deposited film not only depends on the purity of the source materials but also on the substrate cleaning. Ultrasonic cleaner was used in the present work for substrate cleaning. The FTO glass plates were washed with soap solution and rinsed in acetone before use. The process involves successive use of ultrasound baths of distilled water /acetone and the subsequent drying process.

2.2.6 Thin film fabrication

Thin film solar cells are fabricated by coating the window layer material and buffer layer material substance onto an FTO glass substrate using chemical bath deposition technique and spin coating technique. In the process of fabrication, scotch tape is used as a spacer layer to control the thickness of coating. The scotch tape is stuck on the FTO substrate as shown in Figure 2.1 with the required area (1x1 cm^2) of the thin films. After fabrication, the scotch tape is carefully removed and the FTO glass is dried to obtain the thin film.

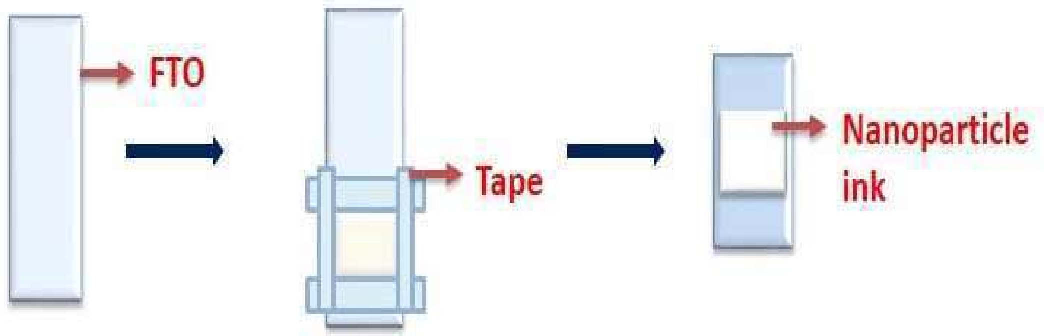

Figure 2.1 Schematic representation of tape struck on the FTO substrate

2.3 MATERIAL CHARACTERIZATION

Characterization plays an important role in the development of novel materials. All the synthesized samples were characterized by different techniques.

2.3.1 X-Ray diffraction

The phase structures of the CMTS (M=Ni and Fe) nanoparticles were identified by recording the X-ray diffraction spectra in the 2θ range of 20 - 80° at a scanning rate maintained at 2° min^{-1} using a Rigaku X-ray diffractometer with CuKα radiation (λ = 1.5406 Å) source.

2.3.2 Raman spectroscopy

The micro Raman spectra were obtained by using a 'Wi Tec alpha 300' Raman microscope in the Raman spectral range from 50 to 4000 cm^{-1}.

2.3.3 UV-Visible spectroscopy

The UV-Vis- NIR spectrum was obtained using Jasco V-570 UV-Vis- NIR spectrophotometer at the wavelength range between 200 nm – 900nm.

2.3.4 FE-SEM and EDAX Analysis

The structural morphology and chemical composition of the samples was analyzed by the Field emission scanning electron microscopy (FE-SEM S410 Hitachi equipment) along with Energy dispersive X-ray spectroscopy (EDAX analysis –Bruker-4010) detector.

2.4 ELECTROCHEMICAL CHARACTERIZATION

Electrochemical characterization is utilized to examine the electrochemical efficiency of the prepared thin film electrode. Electrochemical measurements were done using the electrochemical workstation (SP 150 BioLogic Science Instruments). The two main techniques used to analyze the electrochemical behavior were Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

2.4.1 Cyclic Voltammetry (CV)

Cyclic voltammetry is the widely utilized characterization approach in analytical chemistry for investigation of thermodynamics in a redox reaction, electron transfer reaction kinetics and identification of substrate adsorption behavior on electrode. In electrochemistry it is used to study redox reaction behavior and measurements of specific capacitance and stability of the electrode material. Voltammogram is the curve of the potential (V) versus current density which is obtained by measuring the current at the working electrode at the potential scan rate. Figure 2.2 shows the conventional three electrode set up used to carry out electrochemical measurements in which the prepared material, platinum wire and Ag/AgCl act as working electrode, counter electrode and reference electrode respectively.

Figure 2.2 Conventional three-electrode setup

2.4.2 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy analysis is used to find the ionic conductivity difference between the working electrode surface and electrolyte solution. The AC- impedance is noted in the frequency range between 1 Hz to 100 KHz frequency by applying AC voltage of 5 mV. Electrochemical impedance spectroscopy method is used to study the electron transfer in the electrode/electrolyte solution. The impedance spectrum can be distributed as high, middle and low frequency regions. The impedance plot drawn shows an imperfect semicircle in the high to mid frequency region which indicates the parallel combination of resistance and capacitance. A spike is observed in the low frequency range. Nyquist plot (plotted as Z" and Z') can be optimized with the theoretical simulation and it reveals the electrode's internal resistance, charge transfer resistance and capacitance nature of the material. Simulated equivalent circuit consists of resistors, capacitors and inductors.

2.5 PARAMETERS EXPRESSING SOLAR CELL CHARACTERIZATION

The performance of thin film solar cell is accessed by evaluating the various parameters of the cell such as short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF), efficiency (η), maximum voltage (V_m) and a maximum current density (I_m) of the cell. These parameters are considered to be the significant figures of merit of the device. The open circuit voltage (V_{oc}) of thin film solar cell is defined as the voltage when there is no current flowing through the cell at short circuit. Fill Factor (FF) is a measure of the quality of the cell, and is defined as the ratio between the theoretical maximum power that can be obtained (I_m, V_m) and the measured power (I_{sc}, V_{oc}) as per the following equation,

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}} \times 100 \qquad (2.1)$$

The power conversion efficiency of thin film solar cell is defined as the ratio of electrical power to the optical power incident on the cell, which is expressed as follows,

$$\eta\% = \frac{I_{sc} V_{oc}}{P_{in}} \times FF \qquad (2.2)$$

or

$$\eta\% = \frac{I_m V_m}{P_{in}} \times 100 \qquad (2.3)$$

Where P_{in} is the incident power density which is equal to 100 mW/cm^2, which is termed as 1 sun, under standard AM 1.5 G condition.

2.6 SOLAR SIMULATOR

The solar simulator consists of a Xenon light source. Solar simulator should have good spectral match relative to sunlight, regularity of light sources and high stability over time. There are two main kinds of solar simulators namely 'steady state' (SS) system and the 'pulsed simulator' (PS) system. Pulsed simulators may be operated as single-pulsed or in multi-pulsed mode. The life time of PS system ranges between 40,000 to 1 million flashes, whereas the life time of SS systems range from 1,000-1,500 hours of continuous operation. The flash duration in PS systems is around 2 ms to 10 ms and hence the cell testing time has a very small duration and could produces very less number of data points. Moreover the response to the cell should also be considered in PS systems. In accordance with the standard requirements such as 1000 W/m power and the irradiance of AM 1.5 G are fulfilled by the class A solar simulator. In the present investigation, Photo Emission Tec, Inc. (PET) solar stimulators that are steady state systems based on Xenon lamp technology, providing the closest match to spectral irradiance of sun were used in the analysis of the performance of thin film solar cells. The photograph of the solar simulator set up in the present study is shown in the Figure 2.3.

Figure 2.3 Solar simulator set up for I-V measurements

2.7 THIN FILM CHARACTERIZATION

The performance of thin film solar cell is analyzed by measuring the current with respect to voltage as I-V characteristics during irradiance. A typical I-V characteristic curve is shown in Figure 2.4. When a positive bias is applied to the cathode of a thin film solar cell under irradiation of solar simulation system, two kinds of current are developed at the same instant. One is the current developed due to illumination of the solar source and the other is the current due to the applied forward bias across the device. Altogether the total current is the aggregate of these two different currents. The power of the device can be obtained by multiplying the current and voltage. Moreover, the maximum power of the device can be obtained from the I-V curves. Efficiency of the device can be calculated as the ratio of maximum output power P_{max} to the incident power as in equation (2.3). The quality of the cell is quantified by fill factor, which is the rectangular area covered at the P_{max}. Fill factor if expressed as in equation (2.1).

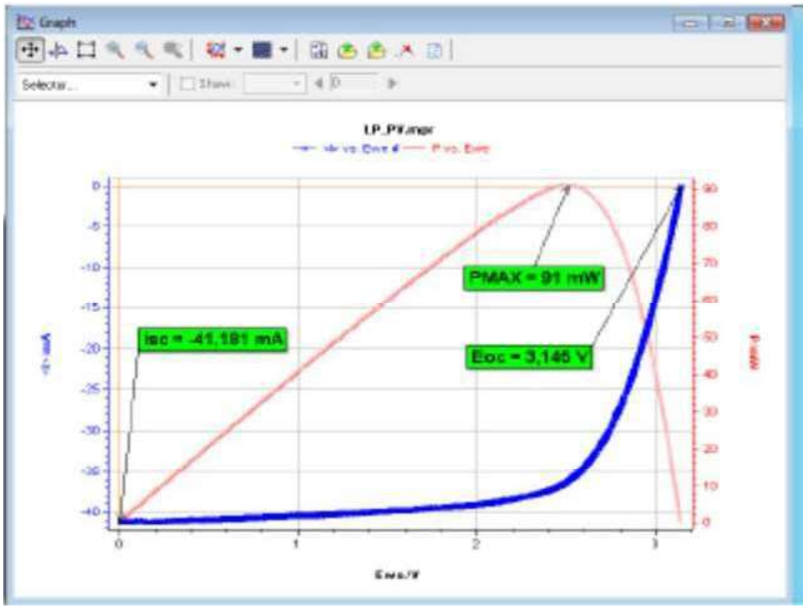

Figure 2.4 Typical I-V characteristics of thin film solar cell

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