Preparation of $CuInS_2$ and In_2S_3 Thin Film for Thin Film Solar Cell Application Using Chemical Spray Pyrolysis Technique

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ABSTRACT

In recent years, the field of photovoltaic has become increasingly important due to rising energy demand and climate change. In particular, thin films of $CuInS_2$ are promising solar absorber materials due to their high efficiencies and low required thicknesses. In this work, $CuInS_2$ and In_2S_3 Thin film deposited onto glass substrate by chemical spray pyrolysis techniques as a route to low-cost and high-throughput for solar cell preparation. Thin films were deposited by changing molar concentrations of the $CuInS_2$ and also Temperature. Structural, chemical composition and optical properties of $CuInS_2$ and In_2S_3 thin films were analyzed by X-ray diffraction, Atomic force microscopy, Hall Effect measurement and UV-Visible spectroscopy. The crystalline size for the $CuInS_2$ thin film corresponding to the (112) orientation is 67.74nm. The optical band gap Eg values of sprayed $CuInS_2$ films deposited at temperatures below 350 °C is 1.87eV. The optical band gap Eg values for In2S3 thin film on glass is 2.83eV.

Keywords: Thin film, band gap, chemical spray pyrolysis.

1. INTRODUCTION TO THIN FILMS

With combination of chemical, physical and mechanical, properties has changed the modern society. There is an increasing technological progress. Thin film materials are the key elements of continued technological advances made in the fields of optoelectronic, photonic, and magnetic devices. The processing of materials into thin films allows easy integration into various types of devices.

The properties of material significantly differ when analyzed in the form of thin films. Most of the functional materials are rather applied in thin film form due to their specific electrical, magnetic, optical properties or wear resistance. Thin film technologies make use of the fact that the properties can particularly be controlled by the thickness parameter. Thin films are formed mostly by deposition, either physical or chemical methods. Thin films, both crystalline and amorphous, have immense importance in the age of high technology.

2. CHALCOPYRITE BASED SOLAR CELLS

Chalcopyrite based solar modules uniquely combine advantages of thin film technology with the efficiency and stability of conventional crystalline silicon cells. It is therefore believed that chalcopyrite based modules can take up a large part of the photovoltaic (PV) market growth .Once true mass production is started. The most important chalcopyrite compounds for photovoltaic applications are CuInSe2, CuInS2, and CuGaSe2 with bandgaps of 1.0, 1.5, and 1.7 eV, respectively. Together with related materials they offer high optical absorption and a wide range of lattice constants and bandgaps. The compounds can be alloyed to obtain intermediate bandgaps. Starting with single crystals, chalcopyrite based solar cells have been under investigation since 1974. The first chalcopyrite cells had a CuInSe2 absorber and therefore the technology is most advanced for lower gap materials with a composition close to CuInSe2. Today the efficiency of lab scale thin film devices is close to 20% efficiency comparable to the best multicrystalline silicon cells. Many scaling up and manufacturing issues have been resolved.

3. EXPERIMENTAL METHODOLOGY

Here, we adopted chemical spray pyrolysis method to deposit $CuInS_2$ and In_2S_3 Thin films on a glass substrate by varying different Molar ratios, temperatures and different values of compressed air pressure.

4. PREPARATION OF CUINS$_2$ THIN FILM ON GLASS SUBSTRATE

Copper indium sulphide ($CuInS_2$) Thin films were deposited by a chemical spray pyrolysis method onto the glass substrates. First, we need to prepare Aqueous solutions of copper chloride ($CuCl_2$) of 100ml-1M, by taking 13.445grams of $CuCl_2$ powder in 100ml di-water and we need to ultrasonicate the above solution for 10min, after that the solution is pour into a glass beaker through filter paper using glass funnel And Then Aqueous solution of Indium chloride ($InCl_3$) of 100ml- 0.1M is prepare by taking 2.211grams of $InCl_3$ powder in 100 ml di-water and we need to ultrasonicate the above solution for 10 min, after that the solution is pour in to glass beaker through filter paper using glass funnel and Then Aqueous solution of thiourea(CH_4N_2S) of 100ml- 1M solution is prepare by taking 7.612grams of CH_4N_2S powder in 100ml di-water and we need to ultrasonicate the above solution for 10min, after that the solution is pour into a glass beaker through filter paper using glass funnel.

After making ready of above three solutions, we prepared precursor solution by varying different Molar ratios i.e., $CuCl_2$:$InCl_3$:CH_4N_2S is taken in 1:1:8 ratio (i.e. 500µl-$CuCl_2$, 5ml-$InCl_2$, 4ml-Thiourea) and 1:1:10 ratio (i.e. 500µl-$CuCl_2$, 5ml-$InCl_2$, 5ml-Thiourea) in 100ml di-water.

Note 1: As per the stoichiometry equation we need to take Cu: In: S2 in 1:1:2 ratio, But in my observation the better film were deposited on glass substrate in 1:1:8 and 1:1:10 ratio, when compare 1:1:2 and 1:1:5(i.e. we absorbed more pin holes through naked eyes).

Note 2: Thiourea should be taken last when we are preparing precursor solution (i.e., at the time loading the precursor solution in precursor solution beaker in spray pyrolysis equipment, because we observed white like substance are formed when we add thiourea first in to the di-water.

Here, we are using 1mm thickness glass as substrate .The glass substrates are cut into 1.5 cm × 2 cm space area. Then are taken in Iso-Propanol and ultrasonicate for 10min, in order to keep the glass substrates clean. So, directly we can place this glass substrate on heater.

5. EXPERIMENTAL SETUP OF CHEMICAL SPRAY PYROLYSIS EQUIPMENT:

Before spraying the precursor solution onto substrate we need to set the parameters of the chemical spray pyrolysis equipment such as heater temperature (-in order to heat the surface of the substrate), flow rate (- which help to set the flow of the solution ml\min), flow factor (-if any error in flow rate we can set it by setting value of flow rate), compressed air pressure kg/cm2 (-it helps to pulverize the spray solution) and x-axis and y-axis of spray nozzle is controlled through the system program (-through xy-position control software).The important thing we need to set when we start spraying is distance between spray nozzle and the substrate. Here we kept 19 cm distance from spray nozzle to substrate (-it plays a major role in deposition of thin film thickness).After that we need to set the program in system software in order to monitor the movement of the spray nozzle in to our desired positions, not only direction we can also set the speed of the nozzle movement. The cleaned glass substrates are kept on heater surface in order to get the substrate heat. The precursor solution was sprayed in air onto glass substrates heated at different temperatures between 340°C and 350°C, with different compressed air pressure values 1.8 and 2.5 kg/cm2, in order to pulverize the solution (**Note**: here if we keep air pressure below this air pressure values, due to less air pressure the spray droplets that are depositing on substrates are large, So deposited film in not good i.e. grain like structures appears on film through naked eye). Here we used spray rate of 6ml\min (-by changing different flow rates we absorbed the films that are deposited, in 6ml\min we find better thin deposition on substrate).Films thickness and roughness was measured by AFM. The structural properties of these films were characterized by X-ray diffraction. Optical properties were monitored by absorbance using UV-Visible spectroscopy.

6. PREPARATION OF IN_2S_3 THIN FILM ON GLASS SUBSTRATE

Indium sulphide (In_2S_3) Thin films were deposited by a chemical spray pyrolysis method onto the glass substrates. First, Aqueous solutions of Indium chloride (InCl2) of 100ml- 0.1M and thiourea of 100ml- 1M is prepared. By taking the indium/sulphur molar ratio in 1:10 (i.e. 5ml-$InCl_2$, 5ml-Thiourea) in 100ml Di-water precursor solution is prepared. Here, we are using 1mm thickness glass as a substrate. The glass substrates are taken in Iso-Propanol and ultrasonicate for 10min, in order to keep the glass substrates clean. Then, the solution was sprayed in air onto glass substrates heated at temperatures between 350°C , with compressed air pressure values 1.8 kg/cm2, in order to pulverized the solution we need compressed air and using spray rates of 1 ml min−1. Films thickness and roughness was measured by AFM. The structural properties of these films were characterized by X-ray diffraction. Composition percentage analysis is performed by using energy dispersive X-ray Analysis (EDAX). Optical properties were monitored by absorbance using UV-Visible spectroscopy. Electrical properties were measured by Hall Effect equipment.

7. RESULTS AND DISCUSSIONS

XRD :

$CuInS_2$ and In_2S_3on Glass XRD :

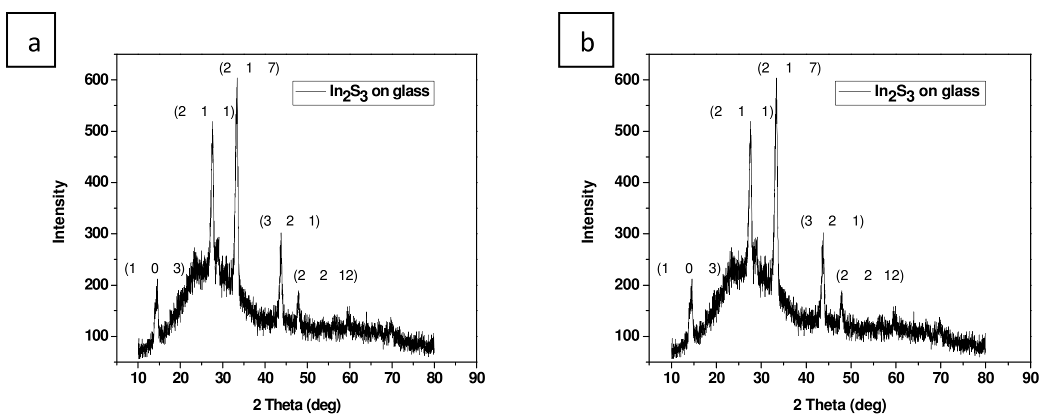

Fig1(a); XRD graph for $CuInS_2$ on glass Substrate, b) XRD Graph for In_2S_3 on glass substrate.

Above fig 1(a) shows the XRD graph for $CuInS_2$ thin film deposited on glass substrate. The obtained XRD pattern was matched with JCPDS No. 032-0339. The 1:1:10 ratio of Cu:In:S_2 is deposited on glass substrate temperature at 350 ºC . The average size of crystallite is estimated by Scherrer's formula. The crystalline size for the $CuInS_2$ corresponding to the (112) orientation is 67.74nm. As the width of the diffraction peak increases, the crystalline size of the sample decreases. Fig.1(b) shows the XRD peaks corresponding to (103) , (211), (217) , (321) and (2212) planes of In_2S_3 clearly observed. The crystalline size for In_2S_3 on glass substrate for corresponding planes is 17.59nm, 67.4nm, 23.89nm, 14.86nm, 38.31nm. The d values coincides of In_2S_3 peaks were coincides with standard JCPDS data (025-0390). The intensity of peak corresponding to (217) plane was observed to be much greater than that of other peaks present, indicating a strong orientation on the (217) plane. The higher intensity peak and FWHM of diffraction peak is very small shows the improvement in crystalanity.

8. OPTICAL PROPERTIES:

$CuInS_2$ on Glass substrate:

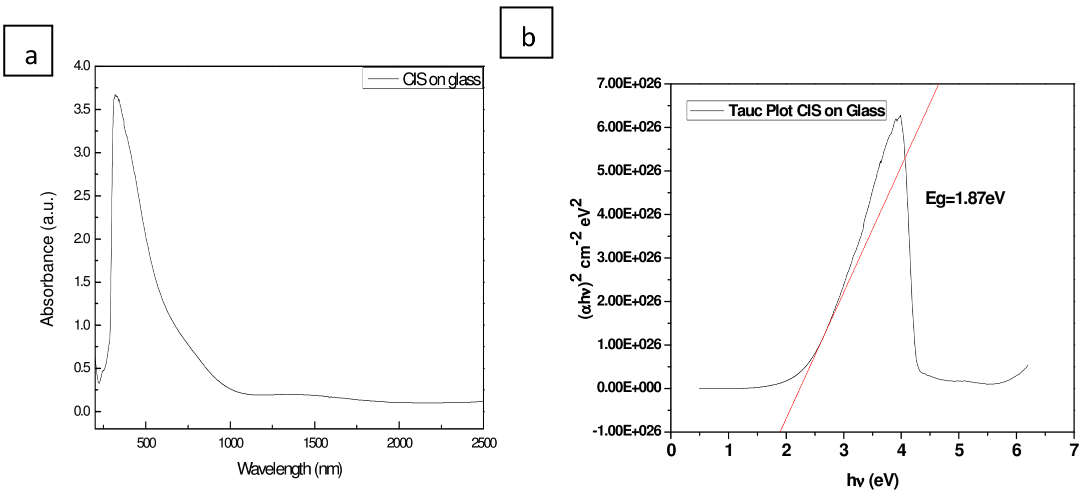

Fig 2(a) : Absorbance Vs Wavelength for $CuInS_2$ on Glass substrate , b) Relationship between $(\alpha h\nu)^2$ and photon energy (hν) of $CuInS_2$ sprayed thin films.

Fig2(a) shows the absorbance Vs wavelength graph. The absorption coefficient and the optical band gap values were determined from transmission data.

Fig 2(b) gives the Eg values corresponding to direct band gap transitions were deduced from the $(\alpha h\nu)^2$ versus the photon energy hν plots extrapolating the straight line from the relatively high absorption region conforming to the well-known Tauc law

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g)$$

where A is a constant related to the effective masses of charge carriers, h is the Planck constant, Eg is the band gap energy, hν is the incident photon energy, and1/n is the exponent that depends on the nature of the optical transition (n=0.5 and 2 for direct and ndirect transition, respectively). Eg values of sprayed $CuInS_2$ films deposited at temperatures below 350 °C is 1.87eV.

Optical property for In_2S_3

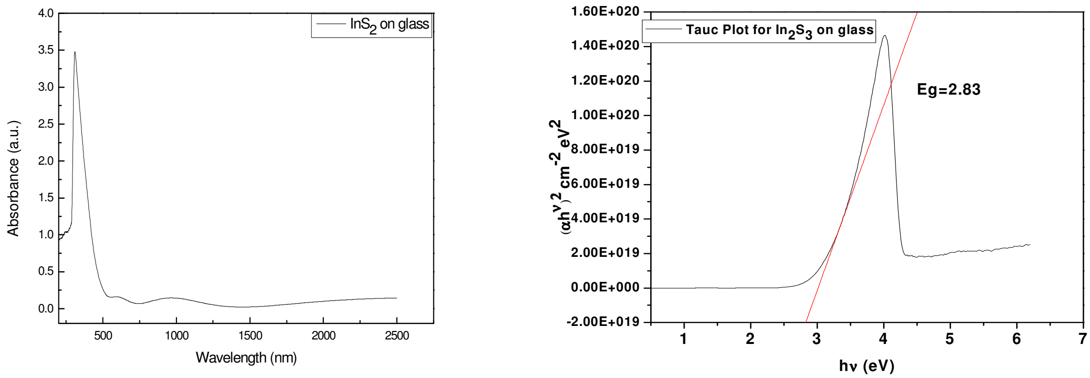

Fig 3(a): Absorbance Vs Wavelength for In_2S_3 on Glass, b) Relationship between $(\alpha h\nu)^2$ and photon energy (hν) of In_2S_3 thin films on glass.

The Eg values corresponding to direct band gap transitions were deduced from the $(\alpha h\nu)^2$ versus the photon energy hν plots extrapolating the straight line from the relatively high absorption region conforming to the well-known Tauc law . The Eg values for In_2S_3 thin film on glass is 2.83eV.

Atomic force microscopy :

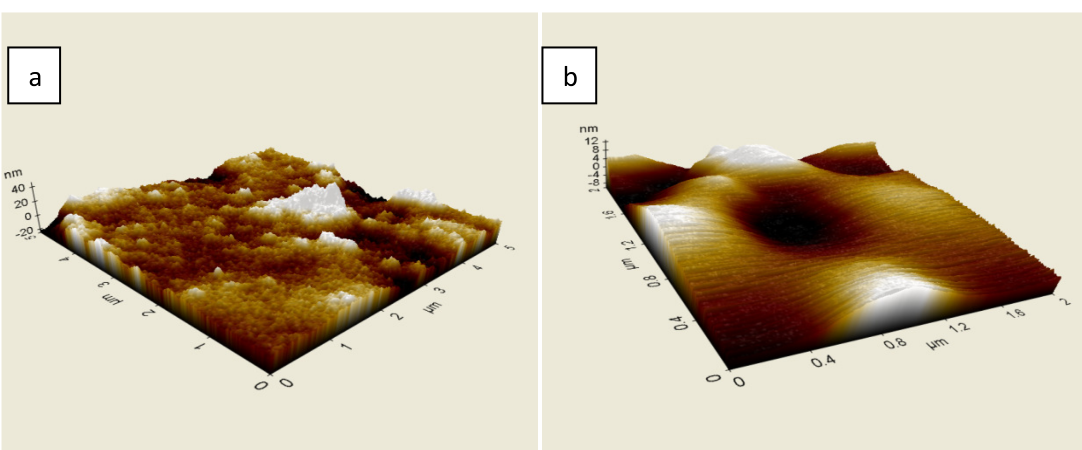

Fig 4(a); AFM 3D image for $CuInS_2$ on Glass Substrate , b) AFM 3D image for In_2S_3 on Glass Substrate.

Fig 4(a) gives the AFM 3D image for $CuInS_2$ on glass substrate. The $CuInS_2$ on Glass Substrate film is well covered to the substrate surface. Average roughness is 20nm. Fig 4(b) gives the AFM 3D image for In_2S_3 on glass substrate, It shows that the film is well covered to the substrate surface. Average roughness is 5nm.

9. CONCLUSION

The obtained XRD pattern was matched with JCPDS No. 032-0339. The 1:1:10 ratio of $Cu:In:S_2$ is deposited on glass substrate temperature at 350 ℃ . The crystalline size for the $CuInS_2$ corresponding to the (112) orientation is 67.74nm. As the width of the diffraction peak increases, the crystalline size of the sample decreases. The crystalline size for In_2S_3 on glass substrate is 17.59nm, 67.4nm, 23.89nm, 14.86nm, 38.31nm. The d values coincides of In_2S_3 peaks were coincides with standard JCPDS data (025-0390). The higher intensity peak and FWHM of diffraction peak is very small shows the improvement in crystallinity. The Eg values for $CuInS_2$ on glass substrate to direct band gap transitions were deduced from the well-known Tauc law. Eg values of sprayed $CuInS_2$ films deposited at temperatures below 350 °C is 1.87eV. The Eg values for In_2S_3 thin film on glass is 2.83eV. AFM 3D images for $CuInS_2$ on Glass Substrate film is well covered to the substrate surface. Average roughness is 20nm. Average roughness for In_2S_3 on glass Substrate is 5nm. Further electrical properties study of thin film is needed and fabrication of solar cell will be doing in future work.

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