Project Report
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Title of the project
Preparation and characterization of thin absorber layer for photovoltaic application

Principal Investigator

Dr. Vimalkumar T.V.
Assistant Professor
Department of Physics
St. Thomas College
Thrissur - 680001
Kerala

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Title of the project

“Preparation and characterization of thin absorber layer for photovoltaic applications”

Aim

The goal of this research proposal is to develop a cost-effective and environmentally friendly thin film layer for optoelectronic application prepared by wet chemical methods. The project covers the deposition of new innovative extremely thin p-type material of Cu$_2$ZnS$_4$ (Copper Zinc Sulphide) over the soda lime glass.

Abstract

In this project report copper sulphide (CuS) and tin doped Copper Sulphide (CuSnS) thin films have been deposited on glass slide substrate via simple and easily controlled method, proceeding large area films, using the wet chemical methods. The structural analysis of the prepared sample were observed using X-Ray Diffraction and the grain size is calculated. The morphological analysis of the CuS thin films were carried out using Scanning Electron Microscope (SEM). The electrical properties like resistivity, conductivity, mobility, carrier concentration etc of the CuS and Sn doped CuS films were studied using hall measurements. The negative Hall Coefficient value indicates that the material is n-type. The optical properties were studied using UV-Visible Spectrophotometer measurements. The band gap energy of the tin doped copper sulphide thin films is greater than the undoped one. The current results gave more importance in the photovoltaic application.

Introduction

During the advent of 20$^{th}$ century, there was a tremendous increase in the demand for smaller, pocket size devices with greater speed and efficiency. This introduced the thin film technology, which reduced the size of the devices from macro to micro and then to nano. The thin film technology basically involves the tuning of properties of substrate materials like metals, ceramics or polymers by properly depositing suitable materials using appropriate deposition techniques. Thin film technology covers a wide spectrum of applications like: Microelectronic devices, Photovoltaic cells, Optical coatings, Sensors, Supra-conductive films, Heat prevention and corrosion resistance etc. A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness [1]. A thin film can be treated as a two dimensional specimen since its third dimension, which is the thickness, is very small compared to the other two dimensions. The physical properties of the material that forms the thin film is different from that of its bulk. The quantity of material used to form the
film is very less compared to its bulk, which reduces the size and cost drastically. These are the factors that insisted the scientists to think of a technology incorporating thin films.

Since a past few decades, wide researches are going on the deposition and characterization of metal chalcogenide thin films. A metal chalcogenide is a chemical compound consisting of at least one chalcogen anion and at least one metal ion (electropositive element). The group 16 elements in the periodic table are defined as chalcogens, but usually we use the term chalcogen to refer to sulphides, selenides and tellurides rather than oxides. Examples of metal chalcogenides are CuS, CdS, ZnS etc. The metal chalcogenide thin films are studied widely due to their large area deposition capabilities and possibility of depositing it on wide variety of substrates.

In our research we are more interested in the study of copper sulphide thin films which finds wide applications in solid state solar cells, opto electronics, electroconductive coatings, selective radiation filters etc. The sulphides of copper is known to have five stable phases at room temperature. They are chalcocite (Cu$_2$S), djurleite (Cu$_{1.96}$S), digenite (Cu$_{1.85}$S), anilite (Cu$_{1.75}$S), and covellite (CuS). These phases are arranged in the order of decreasing copper availability. The covellite form of CuS shows metallic conductivity and recently its ability to transform to a superconductor at 1.6K was also discovered.

**Review of structural studies of cus thin films**

Sunil.H.Chaki et al. [1] reported in their article that the chemically deposited CuS nanocrystalline thin films possess hexagonal structure having lattice parameters, $a=b=3.79\text{Å}^0$ and $c=16.34\text{Å}^0$. A large number of peaks can be observed in the XRD pattern which corresponds to the planes (101), (102), (006), (008), (107), (112), (115), (204), (0012) etc. The crystalline size as calculated using Scherrer’s equation from X-ray diffraction data was nearly 11nm.

The Scanning Electron Microscopy (SEM) results of the chemically deposited CuS thin film shows that the grain size ranges from few µm to nm. The film was found uniform all over the substrate and the films were smooth and homogeneous without visible pores. Elemental analysis of this film from EDAX spectrum showed the presence of copper (Cu) and sulphur(S). The relative atomic percentage ratio of Cu:S was found to be 1 which indicates that the films are almost stoichiometric.
The co-existence of copper and sulphur was reported by Yung-Tang Nien et al. [2] from the EDAX spectrum of the chemically deposited Cu$_2$S thin films. Some large particles were found in the SEM images of Cu$_2$S deposited on Si substrate. When the film was treated at elevated temperatures in an atmosphere of 2 Torr N$_2$, these large particles almost disappeared. They attribute this disappearance to the heavy evaporation or decomposition of solvents added during the deposition. For phase identification X-ray or Electron Diffraction were not suitable since the crystallinity of the deposited film is amorphous. Hence the structure and composition of the material were studied using Raman technique and XPS.

Seppo Lindroos et al. [3] studied the growth of CuS thin films by the successive ionic layer adsorption and reaction method (SILAR) at room temperature and normal pressure. The XRD spectrum showed that the CuS thin film grown on the CdS buffered glass and ITO were polycrystalline and had a hexagonal structure. The film contained (110), (102), (108), (103) and (006) planes. Using Scherrer’s equation the crystalline size was estimated to be in between 50nm and 60 nm.

The SEM analysis showed that the CuS thin films were rather rough compared to CdS thin films. The CuS grains where seen on the 230 nm thick film as needle-like crystals 250 nm long with a diameter of about 50 nm. The cross sectional analysis of the 230 nm thick film presented the film to be compact with no voids. Again they have reported that as the number of growth cycles increases, roughness of the film also increases as it is evident from the SEM images.

E.Guneri et al. [4] deposited chemically, CuS thin films by varying the pH of the chemical bath. The structural analysis of the film using XRD reveals the amorphous nature of CuS thin films. Also it was found that the structural properties were not affected by the variations in pH of the chemical bath. Their ongoing work is based on converting the amorphous nature of this thin film to crystalline nature by annealing it in a nitrogen environment at different temperatures since the defects in the film gets drastically reduced at high temperatures.

The compositional analysis of the CuS thin film using XPS revealed that the atomic ratio of Cu and S in CuS thin films was about 1.09 : 1.10. The AFM images shows that as thickness of the film increases, the roughness of the thin film also increases.

N.Mukherjee et al. [5] reported in their article that CuS thin film deposited had a polycrystalline covellite structure, which was evident from the XRD spectrum which also
reveals that the crystallite sizes were found to be in the range 10-15nm. A high intensity diffraction peak was obtained at 2θ=27.68° from (101) plane and a small diffraction peak at 2θ=47.93° from (110) plane. This indicates the polycrystalline nature of CuS thin film. The article reports that the polycrystalline covellite form of CuS is highly oriented. No characteristic peaks corresponding to any impurities or intermediates are found which implies that the obtained film is highly pure. The full width half maximum (FWHM) of the main diffraction peak so wide which indicates the nanocrystal formation. The crystalline size calculated using the Scherrer’s equation from the XRD data was about 10 nm.

The surface morphological studies using FESEM shows that the film mainly consists of highly compact globular structures in which the globules are composed of spherical particles. The average diameter of the globules were found to be less than 100 nm and the average diameter of the spherical particles out of which the globules are constructed were found to be in the range 10nm to 15nm.

The SEM analysis of the thin film cross section showed that the thickness of the deposited film was about 800 nm. The elemental analysis using EDAX shows that the relative composition ratio of Cu:S was 49.39:50.61.

A.A. Sagade et al. [6] in their research work deposited CuS chemically and made its compositional, structural and surface morphological studies. The thickness of the film was measured to be 200 nm. The EDAX analysis shows that the atomic percentage of the elements in the thin film is in proportion with the volumetric ratio of the elemental precursor chemical solutions taken in the bath. The XRD pattern of CuS contains peaks at 27.61°, 29.25° and 31.81° which corresponds to (101), (102) and (103) planes respectively which reveals the hexagonal (covellite) CuS structure having lattice constants a=3.7918Å and c=16.342Å. They could not identify the peaks obtained for Cu_{1.4}S, since there is no report in the literature hitherto and also no JCPDS cards are available. In the XRD pattern of Cu_{2}S three peaks are obtained at angles 27.61°, 29.25° and 44.93° corresponding to planes (222), (142), (562) respectively. The grain size of CuS, Cu_{1.4}S and Cu_{2}S calculated using Scherrer’s equation from XRD data were about 8nm, 10nm and 13nm respectively.

Scanning electron micrographs reveal that these films are uniform and cover the substrate well. These films are also found to be dense, smooth and homogeneous without visible pores. The surface of CuS and Cu_{1.4}S films consist of nanoparticles of size about 60 nm and 90 nm, respectively. Cu_{2}S film consists of nano discs of approximate diameter of 120 nm. Their
studies support the composition dependency on the surface properties of the copper sulphide thin films.

The presence of highly coordinated spherical nano sized particles well adhered to the substrate are evident from the AFM images of CuS, Cu$_{1.4}$S and Cu$_2$S films.

K.M.Gadave et al. [7] reported a method to prepare Cu$_x$S thin films from a thiosulphate acidic bath. The surface morphology was studied using Scanning Electron Microscopy (SEM). The SEM micrographs shows that the film is uniform and covers the substrate very well. The grain size as calculated using Contrell’s method from the SEM data which ranges between 0.06-0.08 µm.

Jiten Tailor [8] in his Ph.D thesis studied the structural and morphological properties of CuS thin films deposited by chemical bath deposition technique (CBD) and dip coating technique. The X-ray diffractogram analysis using powder- X software shows that all the peaks obtained were indexed to be of CuS phase. The synthesized CuS thin films by both the methods reveals its hexagonal structure with lattice parameters $a=b=3.79$ Å$^0$ and $c= 16.34$ Å$^0$. These results were in good agreement with the standard JCPDS data. Presence of diffraction corresponding to any other phase is not reported which indicates that pure covellite CuS thin films has been synthesized using chemical bath deposition and dip coating techniques. The XRD pattern of the CuS thin film synthesized using chemical bath deposition technique contains large number of peaks than for the film synthesized using dip coating technique, which indicates that the chemical bath deposition synthesized thin films structure possesses more planes than dip coating synthesized thin films. The crystalline sizes of the CuS thin films were calculated using the Scherrer’s equation from the XRD data. The calculated crystalline sizes were found to be 11 nm and 13 nm respectively for the CuS thin film synthesized using chemical bath deposition technique and dip coating technique.

The selected area electron diffraction (SAED) patterns were obtained by transmission electron microscope (TEM). The diffraction rings were indexed and the d values are calculated from the SAED patterns obtained. The obtained planes (104),(107),(108),(204),(0012),(213) for CBD method and (006),(008),(009),(206) for dip coating method matched exactly with the XRD planes.

The surface microstructures were studied using optical microscope. The results reveal that the substrates are well covered by the thin films in both the deposition methods. The dark spots seen all over the thin film may be nucleation over growth.
The surface analysis using Atomic Force microscopy (AFM) reveals the fact that the surface quality of the chemical bath deposition synthesized CuS thin films are poor than that synthesized using the dip coating techniques.

A.D. Dhondage et al. [9] deposited CuS thin films of various thickness using simple and low cost CBD technique. The structural analysis using XRD reveals the polycrystalline nature with orthorhombic (covellite) crystal structure of the CuS thin films. The XRD pattern showed sharp peak corresponding to the plane (113) along with other minor peaks corresponding to (112) and (115) planes. The XRD pattern also shows that the intensity of the peaks increases with the increase in thickness of the film, but no shift in the peak positions were reported. For the high intense peak corresponding to the (113) plane, the crystalline size is calculated using the Scherrer’s equation and the hence determined crystalline size ranges between 30-34 nm for all the samples. No dependence of crystalline sizes on the thickness of the films.

Ajaya Kumar Singh et al. [10] reported the synthesis and characterization of CuS thin films using the chemical bath deposition technique. The structural studies carried out using XRD reveals the crystalline nature of the film with preferred orientation along the (008) plane. The lattice constants are found to be a=4 and c=16 which are in agreement with the standard values. The crystalline size is calculated using the Scherrer’s equation and is in the order of 72.5 nm. The peak obtained in the close vicinity of (004) may be due to the presence of some impurity or due to internal strain present in the film samples.

In the literature most studies are concentrated on the deposition of covellite phase of copper sulphide by various deposition techniques and their characterization. Hence, in this work we are interested in the investigation of doping effects in CuS thin films and tuning its properties.

**Experimental analysis**

**Chemical Bath Deposition (cbd)**

The chemical bath deposition technique involves the controlled precipitation of a compound from a solution on a suitable substrate. It is a simple and low cost technique which do not require any sophisticated instrumentation. The thickness of the film can be controlled by varying the parameters like solution pH, reaction temperature, reagent concentrations etc. The possibility of large area deposition and the reproducibility of the technique make it a widely used one. Most of the metal chalcogenides can be deposited using this technique.
CHARACTERIZATION TECHNIQUES USED

Characterization is an important step in the development of thin films used to investigate the properties of the film that can be brought to application. Characterization techniques for the analysis of thin films comprises of a wide range of spectroscopies. Each one provides unique information about the film which is not available from any other analytical techniques. The complete characterization of a film requires a combination of these different techniques. Hundreds of different characterization tools are available, but only some of them are widely used as general purpose analytical techniques.

The different characterizations include phase analysis, morphological studies, structure determination, compositional analysis, electrical characterization, optical studies etc. In this section, different analytical techniques used to characterize our thin film are described with relevant principles of operation and working.

EXPERIMENTAL PROCEDURE

CHEMICALS USED:

Copper chloride (CuCl₂), Thiourea (CS(NH₂)), Ammonium hydroxide (NH₄ OH)
Tri Ethanol Amine (TEA), Stannous chloride (SnCl₂ · 5H₂O)
These chemicals of the brand Merck where purchased in pure form.

The substrate cleaning process is an essential step in the deposition course for obtaining good adherence and uniformity of the deposited film. The substrate that we use for depositing CuS thin film by CBD technique is the soda lime glass substrate. The steps of the substrate cleaning process is listed below: 1) Washing with basic soap solution 2) Washing with distilled water 3) Rubbed thoroughly with cotton waste 4) Again washed with distilled water 5) Finally the substrate were dried in air and inserted in precursor chemical solution.

Preparation of Copper Sulphide by wet chemical method

Doped CuS thin films were deposited in the glass substrate using the chemical bath deposition technique. The whole deposition process were carried out in room temperature and at normal pressure. The chemical bath in which the substrate is to be immersed is prepared by adding one after the other the made up solutions of the required chemicals in required concentrations and stirring well. The molarity of CuCl₂ was fixed to be 1M where as that of thiourea was fixed as 2M. The required amount of these chemicals were weighed in an
electronic balance and are taken in separate measuring jars and made up to 10 ml each. Now, the chemical bath is prepared by adding 10 ml of 1M copper chloride solution followed by 5 drops of TEA, the complexing agent. To this solution 5 ml of ammonium hydroxide solution are also added to maintain the pH of the bath. After some time, we added thiourea, the source of sulphide ions to the solution mixture and stirred well using a glass rod for a few minutes. Initially a blue color is observed which on constant stirring turns dark yellow. From the literature it is evident that the order of the precursor mixing is very important in obtaining good films.

The pre-cleaned and dried glass substrates are then kept immersed in the chemical bath. The glass substrates were taken out and observed at intervals of 5 minutes and we found that the thickness of the layer deposited, increased initially, within the first half of an hour but after half an hour we could not observe any further increase in the thickness; moreover the deposited layer of the film were getting peeled off. So, we fixed the time for the substrate to be immersed in the bath to be 30 minutes. After every 30 minutes we took the glass substrate out of the bath using a forceps and cleaned it with distilled water. Fresh bath was prepared using the same chemicals of prescribed quantity and the cleaned glass substrates were again immersed in the bath for another 30 minutes. The whole process is repeated for 6 times and the total deposition time was 3 hours. From the literature it was evident that the pristine sample of CuS were obtained under above conditions.

As it was mentioned earlier that this work is basically concentrating on the doping effects of tin in copper sulphide thin films, doping is to be done in the pristine sample of CuS. For that hydrated stannous chloride (SnCl₂·5H₂O) in its pure form is purchased and made up to 0.1 M, 50 ml in a measuring jar. To the above prescribed chemical bath prepared to produce pristine sample of CuS, 2 ml of the made up stannous chloride solution is added and stirred using a glass rod before dipping the glass substrate. The whole process is repeated with different volumes of the dopant solution and investigated the properties of the tin doped CuS thin films.
Results and Discussion

Thickness of the deposited film was found to be 400 nm.

Electrical Characterization:

The Hall Measurement was carried out on CuS and Sn doped CuS thin films deposited by chemical bath deposition in order to evaluate the semiconductor type, mobility and carrier concentration. The different electrical properties of the deposited films measured at room temperature are tabulated below:

<table>
<thead>
<tr>
<th>volume percent of dopant used</th>
<th>conductivity (s)</th>
<th>resistivity ×10^2 (Ω cm)</th>
<th>hall mobility ×10^2 (cm^2 .V^-1 .sec^-1)</th>
<th>hall coefficient <em>r_h</em> (cm^3 .coul^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>29.1</td>
<td>3.42</td>
<td>2.065</td>
<td>-7.08</td>
</tr>
<tr>
<td>2</td>
<td>2.54</td>
<td>29.2</td>
<td>0.121</td>
<td>-4.77</td>
</tr>
<tr>
<td>4</td>
<td>508</td>
<td>0.196</td>
<td>0.022</td>
<td>-4.38</td>
</tr>
<tr>
<td>6</td>
<td>274</td>
<td>0.364</td>
<td>9.21</td>
<td>-3.35</td>
</tr>
</tbody>
</table>

Table.

The carrier concentration calculated using the equation, \( n = 1/(R_H q) \), where \( q = 1.6 \times 10^{-19} \) C is tabulated below:

<table>
<thead>
<tr>
<th>volume percent of dopant used</th>
<th>hall coefficient <em>r_h</em> (cm^3 .coul^-1)</th>
<th>carrier concentration ×10^17 (cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-7.08</td>
<td>8.8276</td>
</tr>
<tr>
<td>2</td>
<td>-4.77</td>
<td>13.102</td>
</tr>
<tr>
<td>4</td>
<td>-4.38</td>
<td>14.269</td>
</tr>
<tr>
<td>6</td>
<td>-3.35</td>
<td>18.656</td>
</tr>
</tbody>
</table>

Table.b

The negative value of the Hall coefficient clearly indicate that the material both doped and undoped are N-type material. The obtained value of carrier concentration are in the range approximately, \( 10^{17} \) per cm^3 confirms that the thin films are semiconductors.

Variation of conductivity and resistivity with volume percent of the dopant (Sn^{2+}) used is shown below:
The conductivity of the doped CuS thin film initially decreases for lower doping percent of tin and increases to a very high value for a doping percent of 4 and decreases again with increased doping percent. Thus the optimized condition to obtain good conductivity is the doping percent of tin be 4. This increased conductivity of Sn$^{2+}$ doped CuS film is attributed to the free electrons generated by the replacement of Cu$^{2+}$ ions by Sn$^{2+}$ ions in the lattice.

**Fig.a**

**OPTICAL CHARACTERIZATION:**

The optical characterization is done using UV-Visible Spectrophotometer. The Absorbance v/s wavelength plot are given below.

**Fig.b**
Fig. 3.3a

Absorbance v/s wavelength graph of Copper Sulphide thin films

Fig. b

Absorbance V/s Wavelength graph of Sn doped Copper Sulphide thin films

Fig. 11 and Fig. 12 shows the absorbance spectrum of CuS and tin doped CuS thin films. In undoped CuS thin film the strong absorption take place in the wavelength range of 350 nm-500 nm. In tin doped CuS thin films strong absorption take place in the wavelength range of 375 nm-475 nm.

To determine the band gap of the deposited thin films a graph is drawn by plotting $(h\nu)$ along X axis and $(\alpha h\nu)^2$ along Y axis. The linear nature of the plot of CuS and Sn doped CuS films indicate that they both are direct band gap materials. The extrapolation of the straight line to $h\nu=0$ gives the value of the band gap. The band gap of CuS film was found to be about 2.55 eV and that of Sn doped CuS film was found to be about 2.9 eV. The band gap of CuS have increased when tin is doped. The increase in band gap energy of CuS thin film on doping...
with tin is attributed to the quantum confinement arising from the lowering of the particle size.

Fig.3.3.c
Bandgap of CuS thin film

Fig.3.3.d
Band gap of Sn doped CuS thin film

Fig 1 (a) XPS analysis of Sn Doped CuS  (b) CuS

Fig.4. (a) AFM image of CuS  (b) AFM image of Sn doped CuS
**Structural Characterization:**

To study the crystal structure and the grain size of the material XRD studies have been carried out on the deposited films. The XRD patterns of CuS film and that of Sn deposited CuS thin film are shown below.

![XRD patterns](image)

**Fig. 2.** (a) XRD of CuS  (b) XRD of Sn doped CuS

The XRD pattern of Sn doped CuS thin film shows three diffraction peaks at 2θ values 29.677°, 31.970° and 41.180° respectively. The maximum intensity peak is obtained at 2θ=41.128°. The grain size calculated using Debye-Scherrer equation is about 29 nm.

The morphological analysis of the deposited thin film is studied using Scanning Electron Microscopy. The SEM images of CuS thin film and the Sn deposited CuS thin film are given below:

![SEM images](image)
The SEM images of both doped and undoped CuS thin films indicates that the films were uniform and covers the substrate very well. It is also evident that the thin films were dense, smooth and homogeneous without visible pores. The grains in CuS thin films are rod shaped and the grain size are in the range of few hundreds of nanometer. While the grains in the tin doped CuS thin films are spherical in shape and the grain size ranges in between 150 nm to 280 nm.

**CONCLUSION**

The doping effects of tin on CuS thin film were studied by depositing doped and undoped CuS thin films on glass substrate using the simple and cost effective chemical bath deposition technique at room temperature. The Hall measurements showed negative Hall coefficient for both tin doped and undoped films indicating that the material is n-type. The carrier concentration range estimated from Hall measurements indicate that both the doped and undoped material are semiconducting in nature.

The optical band gap analysis of both doped and undoped CuS thin films indicate that both are direct band gap materials. The optical band gap of undoped CuS thin film was found to be about 2.5 eV where as that of tin doped CuS film was found to be about 2.9 eV. An Increase in band gap energy is observed on doping the CuS with tin.
The XRD analysis of the CuS thin film and tin doped CuS thin films are conducted. The surface morphological studies using SEM indicates that the synthesized thin films were dense, uniform and homogeneous with no visible pores on the surface.

**FUTURE PLANS**

Analyse the properties of the CuS and Tin doped CuS thin films on annealing in vacuum at different temperatures.

Anneal the sample in an inert atmosphere (nitrogen or argon) and compare with the air annealed sample.

Preparation of CuS and tin doped CuS thin films at different thickness and analyse their properties.

Submitted a paper to Physics letters – Elsevier Editorial System – Under review

**References:**


