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# Investigation of Optical and Electrical Properties of CuZnS Thin Film Deposited by Chemical Bath Deposition Method

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**ABSTRACT:** Most of the present global energy production is accomplished by burning fossil fuels. However, the inherent problems associated with the use of fossil fuels such as their limited availability and the environmental issues forces the mankind to look for new, more sustainable, and long-term and eco-friendly energy source. These entire requirements are fulfilled by only one source "Sun" which is reliable, providing lot of energy from many years and is useful for all living, non-living organisms which has no net effect on environment.

It is one of the most powerful alternative sources for future large scale electricity production. For converting the sunlight energy into the useful form such as electricity, there is need to have some gadgets known as solar cell. These are used for trapping sunlight energy which may be converted into electricity by the phenomenon of photovoltaic effect. The power generated by such solar cells can be used locally and the surplus can be exported to the commercial grid. The possibility for local electricity production offers consumers more freedom by reducing their dependence on the availability and price of commercial electricity. This is a crucial feature especially in remote areas that lack the infrastructure of electrification. Harnessing solar energy has therefore attracted attention of many scientists, technologists, economists, sociologists and politicians.

Numbers of researchers are studying solar cells of different materials with different geometric orientations such as zero dimensions, one dimension, two dimensions etc. The two dimensional material includes bulk and nanocrystalline thin film solar cells prepared using some elemental compositions like II-VI, I-III-VI, III-V etc.

Nanostructure CuZns thin films are among them which has been considered as promising material for solar cell owing to its composition controlled opto-electronic properties. Although there are numerous physical and chemical synthesis methods available in the literature for the growth of nanostructured CuZnS thin films such as successive Chemical bath deposition method. The growth, structural and optoelectrical properties of CuZnS thin films, in order to improve the performance for photo sensor applications.

## I. INTRODUCTION

Over the last few years, the scientific and engineering communities have been making efforts in understanding the Nanoscience and nanotechnology for development of solar cells. The concern about long term stability of the material can be resolved using the Nanomaterial even the work efficiency can also be improved by reducing the size of the material.

Nanomaterial are chemical substances or materials that are manufactured and used at a very small scale. Nanomaterial are developed to exhibit novel characteristics compared to the same material without nanoscale features, such as increased strength, chemical reactivity or conductivity.

Nanotechnology deals with smaller size materials ranging below 100 nanometres. One nanometre ( $10^{-9}$  of a meter) is roughly the length occupied by five silicon or ten hydrogen atoms aligned in a line. At such lower range properties of the material varies drastically than their bulk counterparts, because at the Nanoscale the quantum confinement of the charge carriers and increase in surface to volume ratio occurs. On the basis of dimensionality, these nanocrystalline materials are classified into different categories depending on the number of dimensions in which the material has modulated:



Due to the reduction in the spatial dimension, or confinement of particles or quasi particles in a particular crystallographic direction within a structure generally leads to changes in physical properties of the system in that direction.

In addition to their applied interest, thin films play an important role in the development and study of materials with new and unique properties. Examples include multi ferroic materials. And super lattices that allow the study of quantum. Thin films as a two dimensional system are of great importance to many real-world problems. Their material costs are very small as compared to the corresponding bulk material and they perform the same function when it comes to surface processes.

Cu, Zn, and S is IB, IIB and VIA group element in the periodic table respectively. ZnS is an n-type semiconductor which has a wide band gap ( $E_g \sim 3.7$ ), because of this it has good chemical stability and it attracts a great interest owing to its non-toxicity. The optical band gap of the Cu<sub>2</sub>S thin film can be increased with the increment of Zn<sup>2+</sup> ions.

To synthesis of CuZnS thin film, various methods were used such as successive ionic layer adsorption and reaction (SILAR), metal organic chemical vapour deposition

(MOCVD), DC sputtering, RF sputtering, molecular beam epitaxy, chemical bath deposition (CBD) etc. In present work we used chemical bath deposition because it has no need for any sophisticated instruments; it is inexpensive and low-cost technique.

Nanostructured CuZnS thin films are among them which have been considered as promising material for solar cell owing to its composition controlled opto-electronic properties. Although there are numerous physical and chemical synthesis methods available in the literature for the growth of nanostructured CuZnS thin films such as successive Chemical bath deposition method. The growth, structural and opto-electrical properties of CuZnS thin films, in order to improve the performance for Photosensor applications.

Here in properties of CuZnS thin film have been studied by UV-Visible spectrophotometer. IV study shows that the films are applicable for the Photosensors and absorber layer for solar cells. CuZnS is a new promising material in thin film photovoltaic which is earth abundant and eco-friendly. Its electrical and optical properties can be controlled by varying atomic ratios of Copper and Zinc, so as to use it as absorber or window layers. Type of conductivity of this material can also be changed from n to p by adjusting Cu/Zn value.

## II. LITERATURE SURVEY

Deposition: The act of applying a thin film to a surface is thin-film deposition– any technique for depositing a thin film of material onto a substrate or onto previously deposited layers. "Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometres. Deposition techniques that are used in microelectronic fabrication. If a material like copper or tungsten has to be deposited onto the silicon wafer, there are multiple ways to achieve that goal.

It is useful in the manufacture of optics (for reflective, anti-reflective coatings or self-cleaning glass, for instance), electronics (layers of insulators, semiconductors and conductors form integrated circuits), packaging (i.e., aluminium-coated PET film), and in contemporary art (see the work of Larry Bell). Similar processes are sometimes used where thickness is not important: for instance, the purification of copper by electroplating and the deposition of silicon and enriched uranium by a CVD-like process after gas-phase processing.

Thin Film Deposition is usually divided into two broad categories –Physical Vapour Deposition and Chemical vapour Deposition Coating Systems.

Physical vapour deposition refers to a wide range of technologies where a material is released from a source and deposited on a substrate using mechanical, electromechanical or thermodynamic processes. If the material is taken in solid state, but sent as very small particles or atoms and deposited on the wafer without any reaction, it is called physical vapour deposition (PVD) In general, PVD is used to deposit titanium, titanium nitrate, tantalum, tantalum nitrate, aluminium and a very thin film of copper called seed layer.

Chemical vapour deposition

If the raw material is taken in gaseous form and the final material is deposited on the wafer after reaction, it is called chemical vapour deposition (CVD). CVD is used to deposit tungsten, titanium, again copper seed layer, silicon di-



oxide, silicon nitride, etc. CVD used to produce the highest-purity, highest-performance solid materials in the semiconductor industry today.

Principal:

The basic principle of CVD involves decomposition or partial dissociation of the vapour phase species and their subsequent deposition on substrate or reactions amongst the vapour species in a neutral atmosphere or otherwise and the deposition of the products. Chemical vapour deposition methods - Plasma enhanced chemical vapour deposition, Sol-gel method etc.

Chemical bath deposition technique

Various techniques are available for preparing nanostructured CuZnS thin films, among them chemical bath deposition technique produces uniform, homogenous and large area thin film and even this process is simple, cost effective and eco friendly. The CBD is a simple technique to film formation. It is less expensive and increases the potential in cost reduction of device such as solar cells.

Chemical bath deposition (CBD), or chemical solution deposition (CSD), is a method to deposit thin films and Nanomaterial, first described in 1869. It can be employed for large- area batch processing or continuous deposition. Chemical bath deposition has been used as a technique for preparing films since 1910, Utilization of CBD semiconductors in photovoltaic devices is somewhat recent. In 1933 Bruckman deposited lead (II) sulphide (PbS) thin film by chemical bath deposition, or solution growth method. This technique is extensively used to deposit buffer layers in thin film photovoltaic cells.

The chemical bath deposition (CBD) method is one of the cheapest methods to deposit thin film and Nanomaterial, as it does not depend on expensive equipment and is a scalable technique that can be employed for large area batch processing or continuous deposition. As it is relatively inexpensive, simple and convenient for large area deposition, where the precipitation is controlled through the use of suitable metal complexing agent and the amount of anions in the bath is controlled through the settings of appropriate chemical equilibrium, thin film deposition can take place. The deposition of the thin film takes place through the condensation of the metal and sulphide/selenide ions over the substrate surface.

It does not require sophisticated instrumentation, like vaccine systems and other expensive equipment. It can be carried out in a glass beaker. A hot plate and a stirrer are the equipment needed. The starting chemicals are commonly available cheap. Unlike in electrode position, electrical conductivity of the substrate is not a necessary requirement in chemical deposition. Hence, any insoluble surface to which the solution has free access will be a suitable for deposition. The low temperature deposition avoids oxidation and/or corrosion of metallic substrates. Chemical deposition results in pinholes free and uniform deposits as the solution from which these are deposited and always remains in touch with the substrate. Stoichiometric deposits are easily obtained since the basic building blocks are ions instead of atoms.

The major advantage of CBD is that it requires in its simplest form only solution containers and substrate mounting devices. One of the drawbacks of this method is the wastage of solution after every deposition. Chemical bath deposition yields stable, adherent, uniform and hard films with good reproducibility by a relatively simple process. The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition and temperature of the solution, and topographical and chemical nature of the substrate. Ammonium solution was used to achieve variation in the pH of the reacting medium while EDTA and TEA were used as complexing agents for slow precipitation of cations from their parent compound.

The chemical bath deposition involves two steps, nucleation and particle growth, and is based on the formation of a solid phase from a solution. In the chemical bath deposition procedure, the substrate is immersed in a solution containing the precursors and also film growth can take place by ion-by-ion condensation of the materials or by adsorption of colloidal particles from the solution on the substrate. The preparative parameters are easily controllable and better orientation and improved grains structure can be obtained. The CBD method is processed through nucleation growth.

Synthesis of CuZnS thin film

Various techniques are available for preparing nanostructured CuZnS thin films, among them chemical bath deposition techniques produce uniform, homogenous and large area thin film and even this process is simple, cost effective and user friendly.



Although chemical bath deposition has been used as a technique for preparing films since 1910, utilization of CBD semiconductors in photovoltaic devices is somewhat recent. Nanostructure thin film synthesis can be achieved through two processes either by bottom up or top down approach. In chemical bath deposition technique for nanostructure thin film preparation it follows the bottom up approach.

The chemical method includes two mechanisms (i) ion by ion (heterogeneous reaction) or (ii) cluster by cluster (homogeneous reaction). Although the film properties are mainly concerned with the deposition mechanism but very little attention has been paid for mainly concerned with the deposition mechanism but very little attention has been paid for studying the reaction mechanism taking place during film formation.

To synthesize CuZnS thin film, various methods were used such as successive ionic layer adsorption and reaction (SILAR), metal organic chemical vapour deposition (MOCVD), DC sputtering, RF sputtering, molecular beam epitaxy, chemical bath deposition (CBD) etc. In present work we used chemical bath deposition because it has no need for any sophisticated instruments; it is inexpensive and low-cost technique.

Nanostructured CuZnS thin films are among them which have been considered as promising material for solar cell owing to its composition controlled opto-electronic properties. Although there are numerous physical and chemical synthesis methods available in the literature for the growth of nanostructured CuZnS thin films such as successive Chemical bath deposition method.

### III. EXPERIMENTAL PROCESS

Title: Synthesis of CuZnS thin film by chemical bath deposition (CBD) method Apparatus : Beakers, Heater, Magnetic stirrer, Magnetic needle, Glass slides as a Substrate, pH meter, measuring cylinder etc.

Chemicals:

Copper sulphate, Zinc sulphate, TEA, Thiourea (CS (NH<sub>2</sub>)<sub>2</sub>) and Ammonia (pH adjustor), labolene solution, Distilled water etc.

Experimental details:

Cleaning process of glass substrate

Substrate cleaning is one of the most important steps for obtaining the reproducible Properties of the films. It also affects the stoichiometry, adhesion, smoothness, and uniformity of the film.

The glass micro slides of the dimensions 7.8cmx2.22Cmx0.1cm have been used as the substrates. Chromic acid is used to clean the glass substrate.

- 1) Chromic acid is prepared by adding potassium dichromate (K<sub>2</sub>CR<sub>2</sub>O<sub>7</sub>) by adding concentrated H<sub>2</sub>SO<sub>4</sub>/HCL acid +distilled water (H<sub>2</sub>O).
- 2) The above mixture will stirred for half an hour on magnetic stirrer and heated up to 70 to 80 ° it will form red coloured homogeneous solution.
- 3) Glass substrate will be kept in chromic acid for 1 hour at 70 to 80 degree.
- 4) Then this glass substrate will be removed from chromic acid and washed by distilled water.

Further this glass slide will be digressed by labolene solution (detergent) followed by water and air dried subsequently.

Procedure

- 1) Clean all the apparatus like glass slides, beaker, magnetic stirrer with the help of chromic acid, tap water, labolene solution once again tap water and then distilled water.
- 2) Calculate the equivalent weight of the source material

Equivalent weight = molecular weight x quantity of water x molecular concentration/1000

- 3) Now measure the equivalent weight of CuSO<sub>4</sub> is 0.31, ZnSO<sub>4</sub> is 0.31 and thiourea is 0.09 compound concentration is accurately measured by weight balance machine.



- 4) Then the next condition is the three compounds  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$  and thiourea is dipped in 20ml of distilled water in separately beaker.
- 5) In  $\text{CuSO}_4$  liquid take a magnetic stirrer to stirring it.
- 6) It is great technique to stirring the liquid by magnetic stirrer and stirring to machine is started continued then stirring is to be continued for some time (10 to 15min)
- 7) Then such solutions having added 3 drops of TEA and add ammonia in that solution till gives us transparent solution.
- 8) Now in second beaker  $\text{ZnSO}_4$  liquid take a magnetic stirrer to stirring is to be continued for some time (10 to 15min)
- 9) Then such a solution having added 3 drops of TEA and adds ammonia in that solution till gives us transparent solution.
- 10) Then after  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  solutions is mix and stirrer it for 5 min and add the thiourea in that solution.
- 11) Then added thiourea the pH is measure with the help of pH meter then the heating machine is started to 58 degree and then the glass slides are deposited in this solution.
- 12) To the heating is stated to such a min having 1.30min. the brownish solution is can be made it, and some time we get to a thin film of  $\text{CuZnS}$ .

Then process is stopped and slides are kept out from this solution and lightly washed by distilled water. These complete the experiment we get the thin film of  $\text{CuZnS}$  by chemical bath deposition method.

#### Research methodology

The advancement of science and technology in the recent years has replaced the traditional and laborious experimental techniques of analysis by sophisticated instrumental techniques, which gives more accurate and reproducible results. There are various characterization techniques are available to study the structural, compositional and properties of grown crystals. It is necessary to select an appropriate technique in accordance with:

- Nature of the information, which is required
- The purpose for which the analytical data is required
- The size of sample available and the proportion of the constituents to be determined Since last few decades much attention has been given in the field of II-VI group

semiconducting compound thin films because of their potential opto-electronic properties and applications in household gadgets such as photovoltaic devices, sensors [1] etc. The electrical and optical properties of these semiconducting materials are very sensitive to ambient conditions, depends on deposition techniques used for their synthesis and applications in different optoelectronic devices. Therefore study of such properties with various experimental techniques in order to assess the scope for further improvement in the utility of these II-VI group chalcogenide thin films is a matter of profound importance. Considering these aspects we are critically characterizing the  $\text{CuZnS}$  thin films synthesized by simple chemical bath deposition techniques for photovoltaic applications under the dark and light conditions accompanied with the experimental details pertain to the evaluation of various properties using analytical techniques viz Thickness measurements, structural characterizations using X-ray diffraction (XRD) pattern, surface topography by scanning electron microscopy (SEM), Current-Voltage (I-V) response under dark and illumination condition is a versatile analytical technique for characterizing the

photo-response and photo-sensitivity of the species.

- 1) Annealing process

Post annealing is an important technique in thin film fabrication. Post annealing has lots of advantages. Annealing is a heat treatment process which alters the microstructure of a material to change its mechanical or electrical properties. Typically, large ovens are used for the annealing process.



Most cases, the effect of post annealing on thin film

- 1) Crystalline property and grain size of the films were found to increase after annealing.
- 2) The optical band gap of thin film increase due to the reduction of crystal defect.
- 3) Annealing of thin films improves (increases) the transmission spectra in transparent and medium absorption region thus the refractive index decreases.
- 4) 4) Annealing effect improves the film quality with reduced roughness.
- 5) it can reduce stress/strain generated during fabrication of thin film, provided film is not constrained during annealing,
- 6) It can also affect the bonding between the film and the substrate.
- 2) Characterization techniques

The characterization techniques such as XRD, FESEM, IV and UV - Vis spectroscopy were employed for the study of various characteristic properties of the synthesized nanostructures. The basic principles, schematic representation of the instrument, sample preparation and a brief discussion on the methods of analyses, have been highlighted.

Each of these instruments provides unique information of the synthesized sample which can be correlated, in order to determine the properties of the synthesized nanostructures.

UV –Vis spectroscopy

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. The principle is based on the measurement of spectrum of a sample containing atoms/molecules. Ultraviolet absorption spectra arise from transition of electron with in a molecule from lower level to a higher level. A molecule absorb ultraviolet radiation pf frequency, the electron in that molecule undergoes transition from lower to higher energy level.

Applications

- 1) It is one of the best methods for determination of impurities in organic molecules.
- 2) It is used in determination of molecular weight of a molecule
- 3) It is used in characterisation of aromatic compound and in detection of conjugation.
- 4) The unknown concentration of a solution can be determined using this spectroscopy.

I-V characterisation (current voltage)

I-V response under dark and illumination condition is a versatile analytical technique for characterizing the photo-response and photos-sensitivity of the species. I-V measurement consists of monitoring the change in current to that voltage under ambient condition such as dark and illumination. Thus, I-V response is a display of current versus applied potential.

Applications

- 1) Study the nature of the material whether Photosensor or photovoltaic.
- 2) Estimate process of charge transportation in the material

The simplest technique that uses the photo response under dark and illumination conditions to calculate the energy conversion efficiency of the material. The conversion efficiency is the major of total energy falling on the material and the energy converted to electrical form.



## Results and Conclusion

Fig. CuZnS thin films

The uniform and homogeneous CuZnS thin films were obtained.

## Optical Study

The optical absorbance of CuZnS thin film is determined from the range 300- 800 nm. Fig. shows absorbance as-deposited nanostructured CuZnS thin film.

Fig. 1: Absorption spectra of Nanostructured CuZnS thin film

Fig. shows band gap of nanostructured CuZnS thin film obtained from absorption spectra. A sharp cut off is obtained from absorption spectra at ~380 nm which corresponds to band gap energy of 3.33 eV.

0.0008

0.0006

0.0004

0.0002

0.0000

1.5      2.0      2.5      3.0      3.5

h

Fig. 2: Shows the band gap of nanostructured CuZnS thin film.

## Electrical Characterization

Fig. 3 shows I-V characteristics of as deposited CuZnS thin film in dark & under illumination condition 100 Watt. The photo generated charge carrier's increases with increase in intensity of light which is assigned to the enhancement in photo generated charge carriers. The excitations of valence electrons into the conduction band significantly improve the electrical conductivity of the semiconductors; this phenomenon is known as photoconductivity. Therefore, observing the variation in the IV plots suggests that CuZnS thin film exhibits photosensitive nature.

Fig.3: I-V Characteristics in dark and light of nanostructured CuZnS thin film

## IV. CONCLUSIONS

This work has presented successful growth of CuZnS thin film using Chemical bath deposition techniques. The uniform and homogeneous CuZnS thin films were obtained. The optical study shows sharp band edge in absorbance spectra.





results in band gap of 3.33 eV. The I-V Characteristics of CuZnS thin film has increase photocurrent in illumination condition and decrease the resistance, it shows photosensing nature.

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