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Cu Dopped ZnS Thin Films by Chemical Bath Deposition Method and its Characterization

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ABSTRACT
Materials in the thin film states are common and they play an important part in everyday life. The properties of the material are extensively studied when the material is prepared in thin film form. ZINC SULPHATE(COPPER) thin film is prepared by thin film using chemical bath deposition to find out the thickness of UV - XRD analysis are carry out. The application of thin films to discrete resistors has been reviewed in a number of places. More recent work has been done on thin film resistors in integrated circuit applications.
Keywords:*Zinc sulphate (copper) , UV-XRD, Film resistors.*

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INTRODUCTION
The use of thin films for the construction of resistors goes back at least 50 years When used for the fabrication of discrete resistors, thin films offer improved performance and reliability as compared with resistors of the composition type-and lower cost for comparable performance when compared with precision wire wound resistors. It is in the area of integrated circuitry, however, that thin film resistors have really come into their own. For resistors having minimum dimensions of 5 to 10 mils, fired glazes can compete very well with thin films; but where precision resistors are needed (with dimensions of 5 mils or less), the use of thin films becomes mandatory [1].

SOURCES OF RESISTIVITY IN FILMS
It can be inferred from the foregoing remarks that materials used for resistive thin films should have resistivities in the range 100 to 2,000 µohm-cm. It will be recalled, however, that metals in bulk cannot have resistivities much in excess of the lower limit of this range (as is summarized in Table 1). Bulk semiconductors can readily satisfy these resistivity requirements, but this is invariably at the price of a large negative temperature coefficient. Semi metals such as bismuth and antimony (and their alloys) show about an order of magnitude increase in resistivity over the metals but their low melting points and relatively large temperature coefficients make these materials unattractive for resistor applications.

Table 1 Approximate Maximum Contribution to the Residual Resistivity by Various Types of Defect

TYPES OF DEFECTS	CONTRIBUTION, µohm-cm
Dislocations	0.1
Vacancies	0.5
Interstitials	1
Grain boundaries	40
Impurities in equilibrium	180

Fortunately, many materials, when deposited In film form, achieve resistivities that are significantly higher than their bulk counterparts, without necessarily acquiring large temperature coefficients. Some of the ways in which this comes about include:

CONCEPT OF THIN FILM: All the films have surface thickness and therefore when the thickness of the surface layer is of the order of a fraction of the millimeter this called the thin films. The thin films may be

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The thin films can be deposited add by the following methods. [2]

(i) Blowing methods
(ii) Photolytic methods
(iii) Vaccum Evaporation
(iv) Films formation from solution.

CHEMICAL DEPOSITION TECHNIQUE INCLUDES THE FOLLOWING METHODS

Chemical Vapour Deposition (CVD)

CVD is a chemical process in which the gaseous precursors are used. Precursor gases are moved into a chamber with the substrate. The chemical reaction between thesubstrate and the precursor is continued at high temperature till the desired thickness of the film is obtained.

Plasma Enhanced CVD (PECVD) Method

In PECVD, plasma is formed in a reaction chamber that transforms the gaseous precursors into reactive radicals, ions, neutral atoms and molecules. These atomic and molecular fragments interact with a substrate and this chemical reaction cause to develop a solid layer on the surface at the substrate. In PECVD, lower temperatures (300~350 degrees centigrade) are used for thin film deposition while in CVD high temperatures (600~90 degrees centigrade) are used to develop thin films.

Atomic Layer Deposition (ALD) Method

In Atomic layer deposition, two or more gaseous precursors are used to react with the substrate sequentially one at a time. The thin films obtained by this process are conformal. The process of ALD is divided into two half reactions. These reactions include deposition of precursor and evacuation of the reaction chamber that run in sequence and repeated for each precursor. This chemical reaction occurs on the substrate resulting in the formation of desired film thickness. ALD is a stepwise procedure; therefore it is slower one but can run even on lower temperature.

SOL-GEL METHOD

A sol is a dispersion of the solid particles in a liquid where only the Brownian motions suspend the particles. Suspension of the particles of linear dimension between 1nm and 1um are called colloids which are formed by hydrolysis and polycondensation reactions of metal alkoxides such as the oxides of Si and Ti . These oxides of Si and Ti are called precursors. A precursor is a compound that participates in chemical reaction to produce another compound. Numerous metal organic precursors including alkoxides, carboxylates, diketonates and various organic salts are used to form initially metal complexed solutions but from commercial viewpoint, alkoxides of most metals can be synthesized and are convenient starting materials with respect to availability and cost.
A gel is a state where both liquid and solid are dispersed in each other which presents a solid network containing liquid components. A gel is a porous three dimensionally interconnected semi-solid network that expands in a stable fashion throughout a liquid medium and is limited by the size of the container. A gel is said to be colloidal if the solid network is prepared using colloidal sol particles. The liquid is present between the mesh of the solid network that composes the gel that does not flow out spontaneously and is in thermodynamic equilibrium with the solid network.[3]

ADVANTAGES AND DISADVANTAGES OF SPIN COATING METHOD

Advantages

1.Thickness of the film can easily be changed by changing the spin speed or using different viscosity sol.
2. Films of highly uniform film thickness can be obtained.
3. An advantage of spin coating is that a film of liquid tends to become uniform in thickness during spin off and once uniform, tends to remain so provided that the viscosity is not shear dependent and does not vary over the substrate.

Disadvantages

1. Large substrates cannot be spun at a sufficiently high rate.
2. Another disadvantages is that if the sol viscosity is shear dependent, the lower shear rate experienced near the center of the substrate causes the viscosity to be higher there and the film to be thicker

CHARACTERIZATION OF TECHNIQUE

XRD

X-ray diffraction is a powerful technique to determine the crystal structure and the orientation of the crystal. Various information such as phase identification, crystallinity, crystallite size, lattice constant, molecular orientation and structures can be obtained from XRD.

Derivation Of Bragg's Law

X-ray crystallography is a method of 2Θ determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal cause the beam of light to spread into many specific directions. From the angels and intensities of these diffracted beams, a crystallographer can produce a three dimensional picture of the density of electrons density, the mean position of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information.

Diffraction occurs at all the angels of 2Θ simultaneously in power samples which is shown in above figure. In order to obtain a diffraction pattern, the detector (in most designs) rotates to various 2Θ angles to measure diffraction from the sample. Below is schematic diagram for a powder x-ray diffractometer, showing the rotating detector.[4]

ADVANTAGES AND APPLICATIONS

Very small amount of sample is enough for analysis.
To identify unknown material.
Data interpretation is relatively straight forward.
Study of the structure of nuclei of acids in biological sciences.
Crystal structural analysis in solid state physics/material science.

UV SPECTROSCOPY

UV spectroscopy is type of absorption spectroscopy in which the light of ultra-violet (200-400nm.) is absorbed by the molecule .Absorption of the ultra-violet radiations rests in the excitation of the electrons from the ground state to higher Thvioletradi absorb equal to the energy difference between the ground stand higher energy state (delta E =hf).Generally ,the most favoured transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital.(LUMO). For most of the molecules,the lowest energy occupied molecular orbital are s orbital, which correspond to sigma bonds.The p orbital are at somewhat higher energy levels,the orbital (nonbonding orbital) with unshared paired of elecrons lie at higher energy levels. The unoccupied or anti bonding orbitals are the highest energy occupied orbital is the compounds to the computer.computer stores all the data generated and produces the spectrum of the desired compounds.

PRINCIPLE OF UV SPECTRSCOPY

UV spectroscopy obeys the Beer-Lambertzlaw,which states that; when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decreases of intensity of radiation with thickness of the absorbing solution is proportional to the in cidentradiation as well as the concentration of the solution.The expression of Beer-Lambertz law A= log (I_0/I) =Ec Where, A = Absorbtion I_0= Intensity of the light incident upon sample is =intensity of the light leaving sample cell C =molar concentration of solute L =lengthof sample cell(cm).E = Molecular absorb from the Beer-Lembertz law it is clear that greater the number of molecules capable of absorbing light of a given wavelength ,the greater the extent of light absorbtion.this is basic principle of UV spectroscopy.[5]

INSTRUMENTATION AND WORKING OF UV SPECTROSCOPY

Instrumentation and working of the UV spectrometers can be studied simultaneously. Most of the modern UV spectrometers consist of the following parts light source tungsten filament lamps and hydrogen -deuterium lamps are most widely used and suitable light source as they cover the whole UV region. Tungsten filament lamps are rich in red radiations; more specifically they emit the radiations of 375 nm, while the intensity of Hydrogen -deuterium lamps falls below 375nm.

CHEMICAL BATH DEPOSITION (CBD) METHOD

Chemical Bath Deposition technique involves controlled precipitation of a compound from the solution on a suitable substrate. This technique offers many advantages over the more established vapour phase routes to semiconducting thin films, such as CVD, MBE and spray pyrolysis. The first CBD thin films were prepared in 1884and this method was limited to PbS and PbSe for a long time. After the deposition of a wide range of chalcogenide and chalcopyrite materials have been prepared by this method. In CBD a wide range of substrates such as ebonite, iron, steel, porcelain and brass were specifically used apart from glass. The films were uniform, adherent and able to withstand considerable friction. Around 1980, the focus of CBD films slowly turned towards solar energy applications. One of the earlier developments towards this method was in solar absorber coatings. Application in the field of solar control coatings was suggested in 1989. On the other hand, CBD method has significant advantages over the other methods as follows:

PREPARATION OF IRON PYRITE FILMS USING CHEMICAL BATH DEPOSITION

CBD is a simplest method as no elaborated arrangement is needed and high purity chemicals are not required. These two reasons make this technique a low cost one. The main objective of the present study is to prepare pyrite thin films by using CBD method andby studying the characteristics of the deposited films. In the present work, iron pyrite thin films were prepared using chemical bath deposition method in aqueous solution. This chapter summarizes a brief description of CBD technique along with characterization techniques/instruments used to determine the physical properties of the deposited films.

EXPERIMENTAL SETUP

Chemical bath deposition technique is used to deposit a wide range of compounds. Further, there is a possibility for the preparation of mixed phase films either as consecutive layers or as composites. Many materials such as ZnSe,ZnS, ZnO, CuS , have been deposited across worldwide at various laboratories using this technique. These materials are found to be potential materials for the high efficient solar cells. Therefore, in the present study iron pyrite thin films were prepared using this technique under different deposition conditions such as bath temperature, precursor concentration, complexing agent concentration keeping the deposition time constant at 60 min and pH of the solution at 2.0. [6]

CHARACTERIZATION TECHNIQUES

Characterization of the deposited thin films has a crucial role in the production of any device, particularly in the photovoltaic device. Appropriate techniques were employed in the present investigation to evaluate the physical properties of the films viz., crystal structure, microstructural details, composition of the film, surface morphology, optical, chemical binding configuration and electrical properties to optimize the preparation conditions.

EXPERIMENTAL TECHNIQUES

SUBSTRATE

The surface to which the thin film is deposited in termed is substrate .the surface of the substrate should be flat and smooth to form films .It serves as a mechanical support for the thin film and in electronic application it also serves as an insulator . The need for long term stability makes it imperative that no chemical reaction occur which would change the properties of the films .It should have an appropriate heat conductivity to ensure constant temperature of the surface operation of electronic devices

SUBSTRATE MATERIAL

A number of materials like glasses ,ceramics and quartz are available for use as thin substrate .The nature and surface finish of the substrate materials said adout has the maximum surface smoothness and is also optically plane .It is easily and cheaply available .For the present work , the substrate used is “GLASS”

SAMPLE PREPARATION

PREPARATION OF $ZnSO_4$,KOH,NH_4NO_3,$CS(NH_2)$ and $CuCl_2$

The cadmium chloride, thiourea does not go into solution immediately. The globules of $ZnSO_4$ and $CS(NH_2)$first absorb water, swell and get distorted in shape. So we need temperature and constant stirring to prepare this solution. For that purpose, we make use of magnetic stirrer, the beaker containing water and $ZnSO_4$, KOH, NH4NO$_3$,$CS(NH_2)$ and $CuCL_2$ are placed over the magnetic stirrer. A magnetic pellet is dropped into the beaker and the temperature is set to 75°.

The filed required to rotate the pellet is supplied by the magnetic stirrer. Now switch on the magnetic stirrer. After different times will go into the solution. Using this solution $ZnSO_4$,KOH,NH_3NO_4,$CS(NH_2)$ and $ZnCL_2$ dropped film is prepared.

ULTRA VIOLET (UV)

UV spectroscopy is type of absorption spectroscopy in which of ultra-violet (200-400nm) is absorbed by the molecule. Absorption of the ultra-violet radiations rests in the excitation of the electrons from the ground state to higher thvioletradi absorb equal to the energy difference between the ground stand higher energy state (delta $E^{=}$ hf). Generally, the most favored transition is from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital.(LUMO).For most of the molecules, the lowest energy occupied molecular orbital are s orbitals, which correspond to sigma bonds. The p orbital are at somewhat higher energy levels, the orbital (nonbonding orbital) with unshared paired of electrons lie at higher energy levels. The unoccupied or anti bonding orbitals (pie and sigma) are the highest energy occupied orbitals is the compounds.

Table 2 ULTRA VIOLET (UV)

WAVELENTH	ABSORBTION
330	0.134
360	0.0382
390	0.0315
420	0.0291
450	0.0284
480	0.0257
510	0.0255
540	0.0236
570	0.0249
600	0.024
630	0.0263
660	0.0271
690	0.0277
720	0.0301
750	0.0295
780	0.0352
810	0.0316

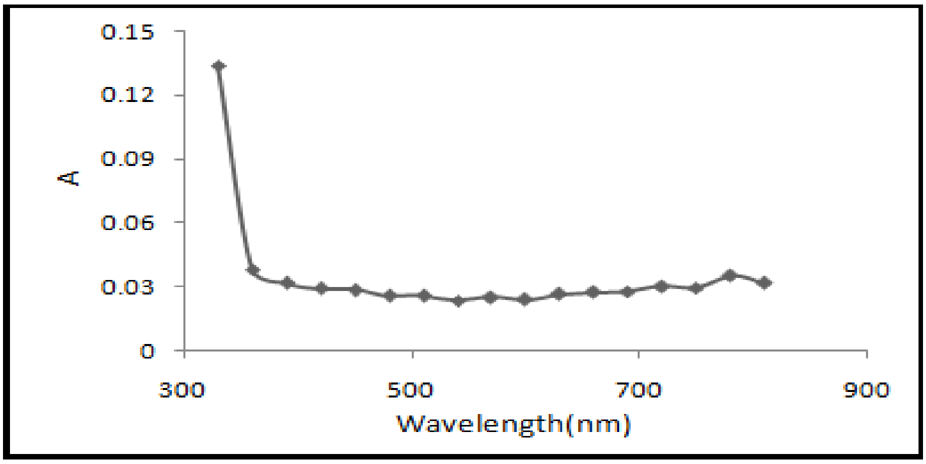

Fig.1Wavelength vs Absorbtion

Table 3WAVELENTH VS TRANSMITTANCE VALUES

WAVELENTH	TRANSMITTANCE
330	73.6
360	91.6
390	93.1
420	93.5
450	93.8
480	94.3
510	94.5
540	94.6
570	94.3
600	94.6
630	94.3
660	94
690	94
720	93.6
750	93.4
780	92.3
810	93.1

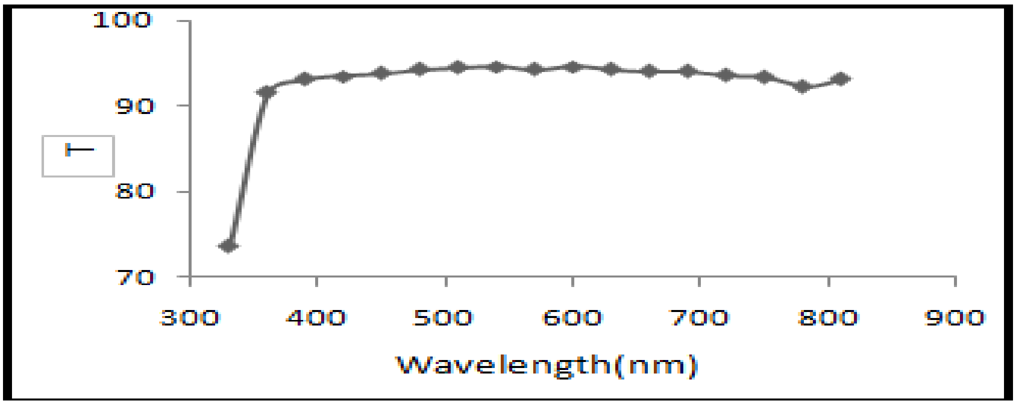

Fig.2 Wavelength vs Transmittance

Table 4 Energy VS αhν*αhν

ENERGY	αhν*αhν
3.766667	1.42E+01
3.452778	1.19E+01
3.187179	1.02E+01
2.959524	8.76E+00
2.762222	7.63E+00
2.589583	6.71E+00
2.437255	5.94E+00
2.301852	5.30E+00
2.180702	4.76E+00
2.071667	4.29E+00
1.973016	3.89E+00
1.883333	3.55E+00
1.801449	3.25E+00
1.726389	2.98E+00
1.657333	2.75E+00
1.59359	2.54E+00
1.534568	2.35E+00

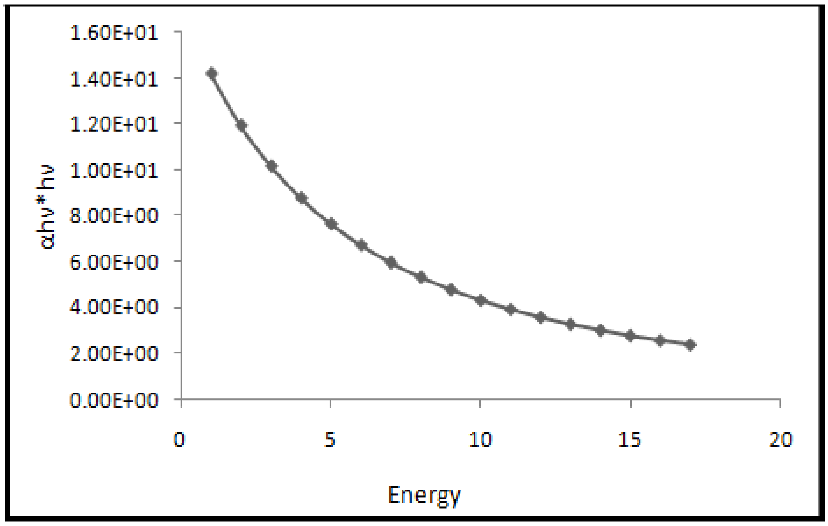

Figure-3 Energy VS αhν*αhν

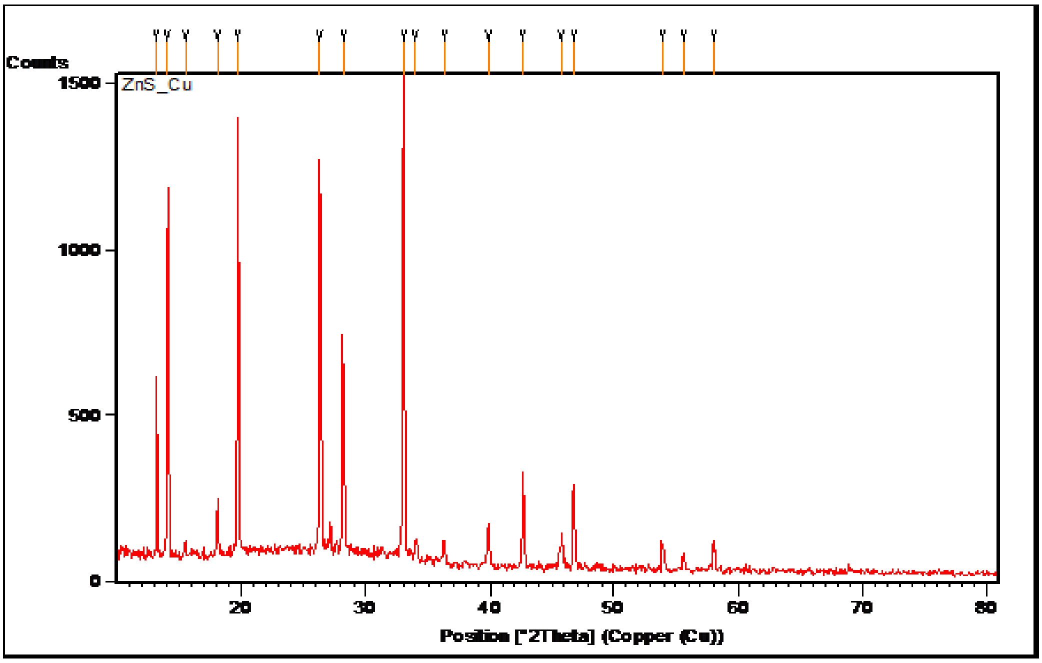

Fig.3 XRD image of ZnS(CU)

RESULT AND DISCUSSION

The ZnS(CU) thin film is deposited on the glass substrate using chemical both deposition method at 80⁰c in three hours. The various characterization techniques searches UV and XRD Fig 1 shows that the plotting of the transmittance against the various wavelength in the range between 300nm to 800nm. The transmittance lies under 73% shown in Fig.1 for the different wavelength.The optical band gab energy is obtain from the plot of $(\alpha \hbar v)^2$ against the photon energyas shown in figure.2 where α is absorption which is calculated from the wavelength data. The optical band gab energy of the Zns (cu) thin film is found to be 0.3 ev as shown in Fig.3 by drawing a straight from the curve to the X-axis (photon energy). The thickness of the film found to be that 575nm. The plot of extinction $\alpha \hbar v * \alpha \hbar v$ against the photon is as shown in Fig.3. From the figure that there is gradually decrease in extinction co efficient with the increasing in the photon energy.

Thus the XRD analysis of ZnS (CU) film is shown in figure.4 The XRD analysis reveals that he ZnS (CU) thin film has hexagonal crystalline structure. This analysis also shows that the ZnS (CU) film on the substrate this amorphous are consists of small grains. It is found that the ZnS (CU) film deposited on the substrate has poor space crystallanity. However the ZnS (CU) film is microcrystalline and it consists of mixed phases of β (cubic) and v (hexagonal).

CONCLUSION

Synthesization of ZnS (CU) thin film has done by using glass substrate by chemical bath method [CBD].it has cost consumption, easy construction and uniform coating materials. The temperature is kept at 80⁰C though out the deposition process of 3 hours. The linear nature of absorption indicacates that ZnS (CU) is a direct band gap material with the band gap energy equal to 0.3eV. The XRD image of the ZnS (CU) thin film gibes the information about the crystalline structure prepared thin film. It confirms that the film has hexagonal crystalline structure. It also shows that the film is a amorphous. This ZnS (CU) film can be also used as the UV reflectors and also the CDS ZN thin film has been used as various techniques such as highly reflecting coating mirrors. It can be used as photo detectors, optical mirrors, LCD, LED. It can be also used in decorative coatings.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest

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