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Comparative studies on synthesis and characterization of Nano crystalline Ag_2s thin films by CBD and M-CBD method

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Abstract
Nano crystalline semiconducting Ag_2S films have been prepared onto corning glass substrates using chemical bath deposition (CBD) and modified chemical bath deposition (M-CBD) methods. In chemical bath deposition (CBD), preparative parameters such as concentration, deposition time, complexing agent and pH of the bath are optimized, while in modified chemical bath deposition (M-CBD) preparative parameters such as concentration, immersion cycles, immersion time and rinsing time were optimized. The comparative Physical properties study of CBD and MCBD deposited is carried out. The deposited films were characterized by different characterization techniques to study structural, surface morphological, optical and electrical properties. Comparative. The structural studies show that, the formation of Ag_2S thin films with an average crystallite size of 25.61 nm by CBD and 21 nm by MCBD. Optical studies show a direct band gap 1.78 eV by CBD and 2.09 by MCBD. The room temperature electrical resistivity is of Ag_2S thin films is 1.4 x 10^5 Ω-cm for CBD and 2.76 x 10^5 Ω-cm M-CBD method. The films exhibit electrical conductivity as seen by thermo-emf measurements indicating that Ag_2S is n-type semiconductors.

Keywords: Nano crystalline, thin films, Ag_2S, CBD and MCBD

1. Introduction

The study of solid state chemistry generally deals with experimental investigations and theoretical interpretation of the various physical properties of matter in solid phase. In the recent century, the properties at the nanoscale have become important due to increased industrial applications and tremendous development in electronics and computer technology. The basic requirements for such studies are the knowledge of structure, bonding and characterization of the electrode-electrolyte interaction. In present days the applications of nano-materials extends to wide ranging areas such as catalysis [1], bio sensing [2], drug delivery [3], diagnosis [4], solarcells [5], optoelectronics devices [6], photonic band gap materials [7], non-linear optical devices [8] etc.

In recent years, metal nanocrystlline semiconducting thin films have received much attention due to their applications in various fields of science and technology. Metal nanoparticles have attracted extensive interest because of their unique size-dependent optical [9-10] and electronic properties [11-12]. Because of the small particles size, semiconductor nanoparticles may show quantum confinement, a phenomenon, which arises due to the fact that the electronic energy levels do not form a continuous set but rather discrete in nature [13]. Hence, emissions from excited nanoparticles tend to show size-dependent vibrational frequencies. This property makes most nanoparticles useful in memory storage, sensor and electronics technologies [14]. An interesting aspect of nano-materials is the number of various factors that could influence their observable properties only to make them applicable in their various aspects of day to day life. The change in observable properties of nano-materials such as color, optical and electronic behavior, and magnetic response is due to the facts that as the size approaches atomic dimension, energy level bands are slowly transformed into quantized discrete energy levels. Since the changes in the electronic structure occur in the nanometer region, it gives an insight as how properties changes from molecular levels or atomic level to bulk. Further the decrease in size would confine the electronic motion, which will affect the chemical and physical properties of the materials [15]. The quantum size effects are studies in case of semiconductor nanomaterials which predicts how energy level spacing of nanomaterials depend on nanopartical radius [16].

The decrease in size increases the effective band gap of semiconducting nanopartical, increases the blue shift in observed absorbance and emission spectra. The advantages of nanomaterials due to size of nanoparticals are the large surface to volume ratio of corresponding materials compared to its bulk counterparts. The large surface area makes nanoparticals to be more reactive, facilitates number of applications of nanomaterials.

Silver sulfide (Ag_2S) is an important chalcogenide compound which has been investigated for its numerous applications. Silver sulphide (Ag_2S) belongs to I–VI compound semiconductor materials with monoclinic crystal structure. Silver sulphide appears to be a promising material for conversion of solar energy into electrical energy as its band gap is in between 1-2 eV. The semiconductor silver sulfide has photoelectric and thermoelectric properties [17-18]. Silver sulphide (Ag_2S) has been used in IR detectors [19], photoconductors, photovoltaic cells, electrochemical storage cells [20-21], etc. It is also well known as a mixed ionic and electronic conductor at high temperatures above 200^0C. Considerable efforts on synthesis and characterization of silver sulphide have being done and their potential application areas have being developed. Various techniques such as chemical bath deposition (CBD) [22-23], spray pyrolysis deposition (SPD) [24], successive ionic layer adsorption and reaction (SILAR) [25], molecular beam epitaxy (MBE) [26], thermal evaporation [27], sol-gel and ion implantation techniques [28], gamma irradiation [29-30] etc. have been reported for the preparation of silver sulphide thin films. Among these, chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) has become the favored route because of its simpleness, low cost, scaleablity and reproducibility [31]. In this chapter, we report on comparative study of structural, surface morphological, optical and electrical properties of a simple chemical bath deposition and modified chemical bath deposition techniques selected to prepare silver sulphide (Ag_2S) thin films with the use of common and inexpensive chemicals for the bath, as well as a basic characterization of the as-deposited material.

2. Experimental details

Loba analytical reagent grade silver nitrate and thiourea were used for the synthesis of nanocrystalline Ag_2S thin films by CBD and M-CBD as reported previously [32, 33]. The Ag_2S films were grown by CBD and M-CBD method on corning glass substrate (75mm X 25mm X 1.35mm) from an alkaline bath. The silver nitrate [($AgNO_3$], thiourea [CH_4N_2S] and liquor ammonia were used as starting chemicals. Double distilled water is used for preparing solutions.

3. Characterization Techniques

The nanocrystalline Ag_2S thin films prepared at optimized preparative parameters were characterized using techniques like X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy dispersive X-ray analysis (EDAX) spectroscopy, UV-Vis-NIR, optical absorption spectroscopy and electrical resistivity measurement technique. X-ray diffraction patterns of the film were recorded on Model Bruker D8 advance AXS X-ray diffract meter with scanning angles in the range 20-80 degree using CuKα radiation (λ=1.5406 Å). The surface morphology was studied by scanning electron microscopy (SEM) using a Model JOEL, JSM 6360A. Energy dispersive X-ray analyses (EDAX) were recorded on Energy dispersive X-ray spectrometer attached to the SEM. The optical absorption spectrums of the films were recorded using an UV-Shimadzu scanning spectrophotometer. The electrical resistivity measurement was carried out using a DC two point probe method.

4. Results and discussion

4.1 X-ray diffraction (XRD)

Fig. 1-A and 1-B shows the XRD diffraction pattern of as deposited Ag_2S by CBD and MCBD thin film onto glass substrate. The x ray diffraction studies show that Ag_2S film is nanocyrstalline in nature. In the diffraction pattern, four dominant peaks at 28.95º, 33.56º, 36.89º and 40.82º corresponding to (111), (120), (121) and (031) planes are seen with polycrystalline monoclinic (acantite) crystal structure. The average crystallite size was calculated by using well known Debye-Scherrer's formula of full width of half maxima (FWHM). The calculated average crystallite size was 25.61 nm for Ag_2S thin film grown by CBD. The XRD pattern of the as deposited film indicated that the Ag_2S thin film grown by MCBD is Nano crystalline with monoclinic (acanthite) crystal structure. The average grain size of Ag_2S thin film was found to be about 21 nm.

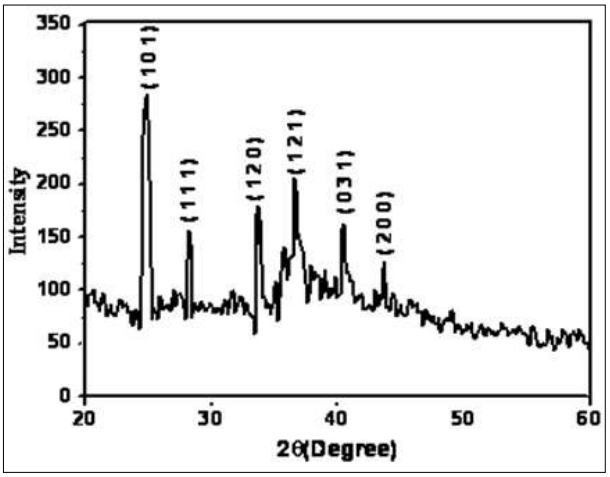


Fig 1-A

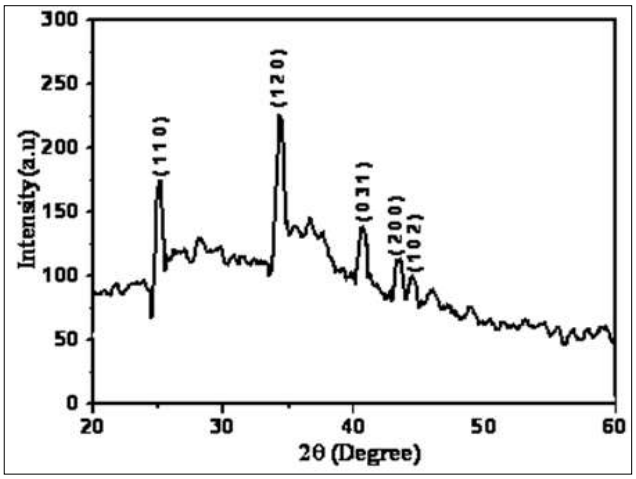


Fig 1-B

Fig 1-A & 1-B: Shows the XRD pattern of Ag_2S thin films grown By CBD and M-CBD respectively

4.2 Energy dispersive X-ray diffraction (EDAX)

The quantitative composition of Ag_2S film deposited on glass substrate was determined using EDAX technique. A typical EDAX pattern of Ag_2S by CBD and MCBD is shown in Fig. 2-A & 2-B. The EDAX Spectrum shows the presence of silver and sulphur. The presence of Si peak is due to glass substrate.

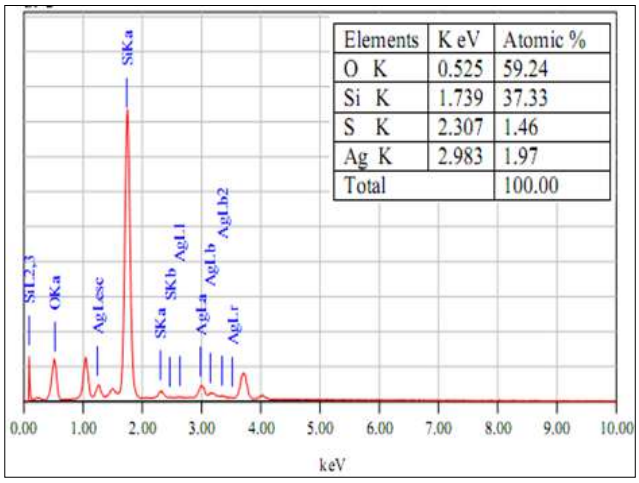


Fig 2-A

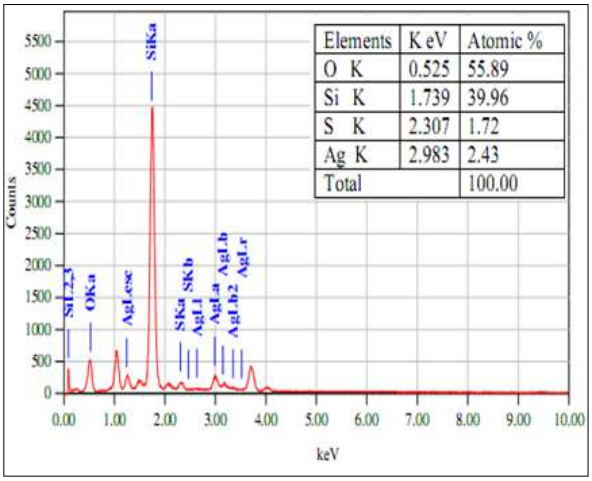


Fig 2-B

Fig 2-A & 2-B: Shows the EDAX spectrum of Ag2S thin film grown By CBD and M-CBD respectively

4.3 Scanning electron microscopy (SEM)

The Ag_2S thin film deposited on to glass substrate by CBD with 130 nm thickness was used for study of microstructure using Scanning electron microscope. Fig. 3-A shows a scanning electron micrograph of Ag_2S thin film deposited by CBD at 30,000 X magnification. The scale bar length is 0.5 µm. Fig. 3-B shows the Scanning electron micrograph of Ag_2S thin film by MCBD at magnification 30,000 X. Films are found to be Nano crystalline. Ag_2S thin film deposited on to glass substrate with 135 nm thickness was used for study of surface morphology. The scale bar length is 0.5 µm.

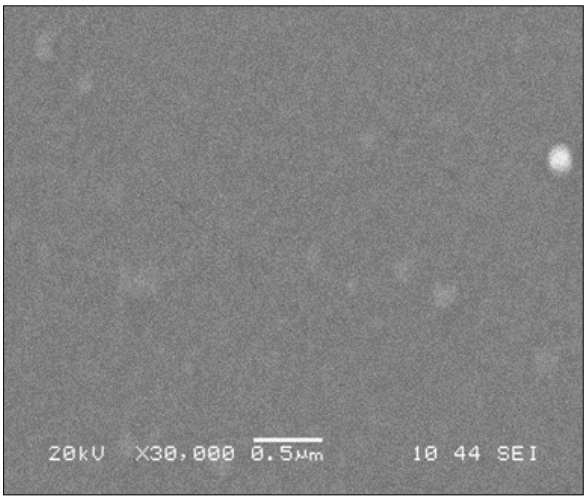


Fig 3-A

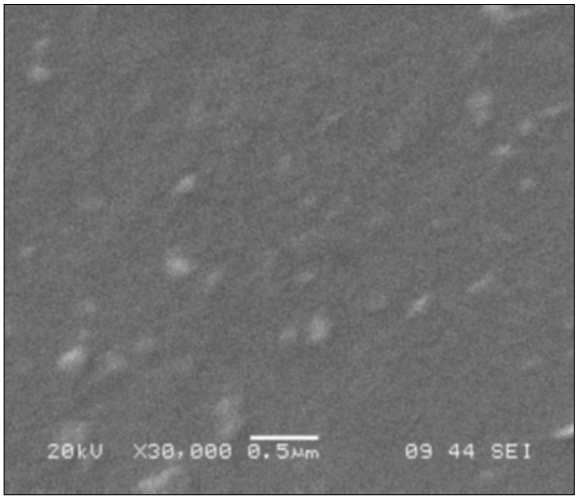


Fig 3-B

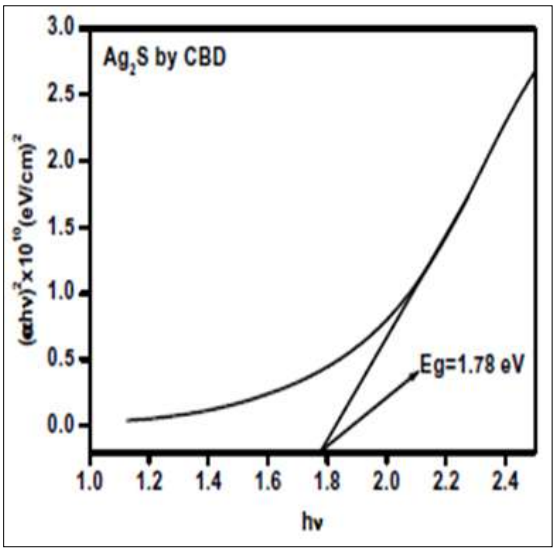
Fig 3-A & 3-B: Shows the SEM pattern of Ag_2S thin films grown By CBD and M-CBD respectively

As deposited films grown by CBD and M-CBD seems to be composed of large number of nanosized small particles. The micrograph reveals that the film is well adherent, homogeneous and well substrate covered without any cracks or pinhole. Some of the grains show an agglomerate morphology. Hence it clearly shows that the growth of Ag_2S films takes place via cluster-by-cluster deposition.

4.4. Optical absorption

Optical properties of Ag_2S by CBD and M-CBD thin film were calculated with the help of optical absorption. The optical absorption of Ag_2S thin film on glass substrate was studied in the wavelength range 300-1100 nm.

The band gap was determined of Ag_2S thin films grown by CBD from fig 4-A the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus hυ graph shown in Figure. The variations of $(\alpha h\upsilon)^2$ verses hυ is a linear at the absorption edge confirm that the Ag_2S is a semiconductor with direct band gap. The as-deposited Ag_2S thin film shows the optical band gap 1.78 eV. Fig. 4-B shows a plot of $(\alpha h\upsilon)^2$ versus hυ, which is linear at the absorption edge, confirming that the material has a direct band gap. Extrapolation of the curve on energy axis for zero absorption coefficients gives the value of optical band gap energy. The optical band gap energy of Ag_2S by MCBD Eg = 2.09 eV.



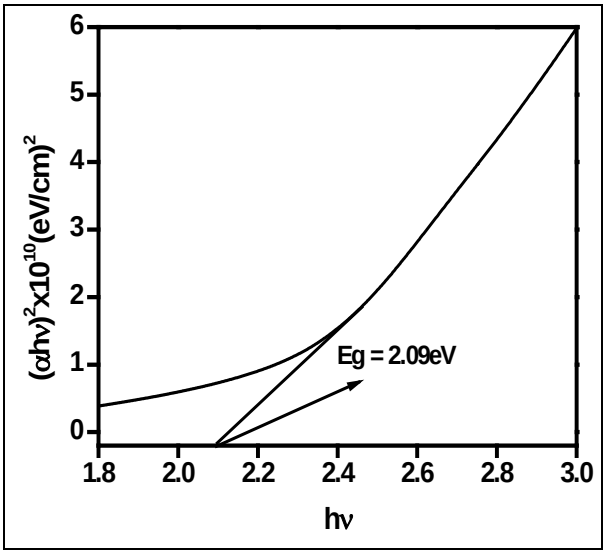


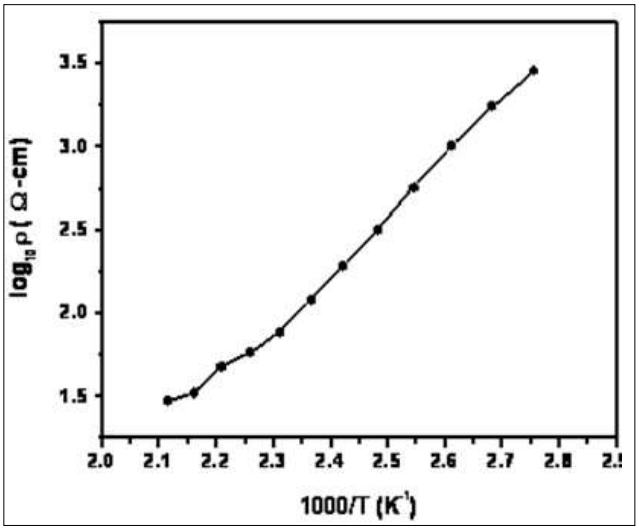
Fig 4-A **Fig 4-B**

Fig 4-A & 4-B: Shows Variations of $(\alpha h\nu)^2$ with hν of films grown By CBD and M-CBD respectively

4.5 Electrical resistivity

The dark dc electrical resistance of the Ag_2S film grown By CBD and M-CBD was measured in 300-600 K temperature range. Fig. 5-A & 5-B shows variation of LN ρ with inverse of absolute temperature for silver sulfide thin films.

The electrical resistivity of Ag_2S film decreases with increase in temperature indicating the semiconducting nature. It is observed that the LN ρ versus 1000 / T curve for Ag_2S film shows linear portions. Electrical resistivity was found to be of the order of 1.4 x 10^5 Ω-cm for CBD and 2.76 x 10^5 Ω-cm M-CBD.



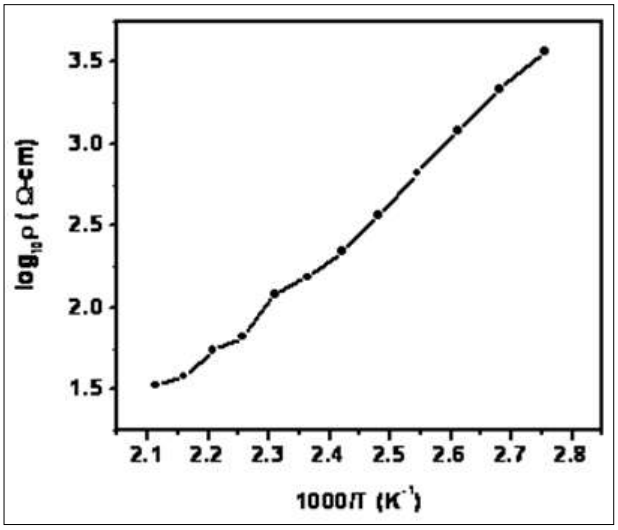


Fig 5-A **Fig 5-B**

Fig 5-A & 5-B: Shows the variation of logarithm of resistivity (log ρ) with the inverse temperature (1000/T) of thin films grown By CBD and M-CBD respectively

4.6 Thermoemf

The type of electrical conductivity exhibited by Ag_2S thin films grown By CBD and M-CBD is determined by thermo-EMF measurement. The polarity of thermally generated voltage at the cold end was negative indicating that Ag_2S is n-type semiconductors

5. Conclusion

Ag_2S thin films were obtained from the aqueous bath using chemical bath deposition (CBD) and modified chemical bath deposition (MCBD) methods. The structural studies show that, the formation of Ag_2S thin films with an average crystallite size of 25.61 nm by CBD and 21 nm by MCBD. Optical studies show a direct band gap 1.78 eV by CBD and 2.09 by MCBD. The room temperature electrical resistivity is of Ag_2S thin films is 1.1 x 10^5 Ω-cm for CBD and 2.76 x 10^5 Ω-cm M-CBD method. Due to larger grain size, the CBD grown films have low resistivity than MCBD grown films. The films exhibit electrical conductivity as seen by thermo-emf measurement

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