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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION STUDY OF $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ COMPOSITE THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION TECHNIQUE

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Abstract

The ternary thin films of composite $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) have been deposited by simple chemical bath deposition (CBD) technique on glass substrate. The thin films have been deposited at optimized conditions pH at 10 ± 0.1 , bath temperature 65°C , deposition time 120 minutes. The films were uniform and adherent to glass substrates. They were characterized by structural, optical, and electrical measurement techniques. According to their X-ray diffraction patterns $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) films are crystalline with band gap of 2.4 eV. Scanning electron micrographs showed that the substrates were well covered with films; no cracks or pinholes were observed. The electrical resistivity of the films is found to be $1.3703 \times 10^3 \Omega\text{-cm}$ to $2.1243 \times 10^3 \Omega\text{-cm}$ at temperature range 303°K to 423°K . According to thermoelectric power measurements $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) thin films are of n-type nature.

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Introduction:-

The nanocrystalline $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) (HGS) thin films, have been of interest due their semiconducting nature and considerable application in the field of electronics and electro-optical devices [1,2] magneto-optical devices and in magnetocapacitive as well as magnetoelectric devices [3-11]. Based on this concept, intensive research has been performed in the past to study the synthesis and characterization of these thin films. The characteristics of these films provides an overview of several capabilities based on photon, electron, and ion methods that can be effectively used to understand the structural, chemical, and electronic characteristics of a wide range of materials. The type or types of information required determines the characterization methods needed to investigate thin film. XRD is an excellent technique for studying thin films with a crystalline structure, such as those composed of inorganic/solid-state materials. XRD is a technique used to determine the crystalline structure and atomic spacing of a thin film, and the produced spectral pattern is compared against known references. XRD fires collimated X-rays at a crystalline sample, and the light becomes diffracted according to Braggs law by the crystal planes within the thin film. The X-rays are produced by a cathode source and are monochromated. Upon hitting the planes of the thin film, constructive interference is created, causing the sample to be scanned through an angle of 2θ and allowing all of the dimensions of the film to be observed is a tool used to characterize the morphology and composition of thin films. Electrons are fired from an electron gun and pass through the thin film. The energies of the electrons are concentrated and focused on using a series of lenses. The electron beam then passes through a pair of scanning coils and deflector plates in the final lens. After the electrons are focused, they are then directed towards the thin film. When the electrons interact with the sample, their energy diminishes due to scattering and absorption. The exchange of energy between the

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electrons and the sample causes high energy electrons to reflect through elastic scattering. Secondary electrons are also released by inelastic scattering and the emission of electromagnetic radiation, both of which are detected. The image is a distribution of the signal intensity, which is digitally captured and allows for the structure of the thin film to be determined. The doping of nanocrystalline semiconductors with trivalent magnetic material Cr^{3+} results in new optical, electrical and structural properties. Mercury chromium sulfide is a metal chalcogenide semiconductor of the group II-VI semiconductors having an insulating and high density with excellent structure [12-13]. The chromium (III) is quite stable against oxidation in sulfides, removing mercury from the material remains a significant challenge [14]. The formation of solid phase from a solution involves two steps as nucleation and particle growth. The size of particles of a solid phase is independent upon the relative rates at which these two competing processes take place. For any precipitate, there is some minimum number of the ions or molecules required to produce a stable phase in contact with a solution, called as nucleus. The formation of nucleation is necessary for a precipitate formation. The concept of nucleation in solution is that the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film. Depending upon deposition conditions such as bath temperature, stirring rate, pH, solution concentration etc. the film growth can take place by ion-by-ion condensation of materials or by adsorption of colloidal particles from the solution on the substrate. CBD is one of the convenient processes in which compound ternary semiconductor thin films of typically $0.02^{-1} \mu\text{m}$ thickness are deposited on the substrate immersed in dilute baths containing metal ions and in a source of sulfides or selenide ions. In the process, metal ions in the solution reacted with slowly released sulfide ions to form a solid film on the substrate. This technique is suitable for coating surfaces of any morphology and geometry. The HGS films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors etc. Mercury sulphides is a direct band gap ($\sim 2.45\text{eV}$) semiconducting material for applications as IR detection [15-17], ultrasonic transducers, image sensors, electronic imaging materials and photoelectric conversion devices [18]. The thin films of HgS can also be used in storage cell with CdSe, solid state solar cells, photoelectrochemical cells and photodetectors [19-20]. Deposition of these films by vacuum evaporation, sputtering and chemical methods such as chemical vapour deposition, spray pyrolysis, electrodeposition, anodization, electro conversion, electroless, dip growth, successive ionic adsorption and reaction, chemical bath deposition and solution-gas interface techniques are well known [21-27]. Using this deposition methods, a large number of binaries such as CdS, CdSe, Bi_2S_3 , Bi_2Se_3 , PbS, PbSe, As_2S_3 , Sb_2S_3 , Ag_2S , CuS, ZnS etc. and ternaries such as CdZnS, CdSSe, CuInS_2 , CuInSe_2 , PbHgS , CdPbSe etc. have been deposited as thin films. The so prepared thin films are pin hole free and uniform deposits are easily obtained since the basic building blocks are ions instead of atoms.

The aim of our work is to investigate the growth procedure with respect to the feasibility of HGS crystalline thin films from alkaline medium at mild reaction conditions. A di-sodium salt of ethylene-diamine tetra- acetic acid (EDTA) was used as a complexing agent to form homogeneous HGS thin films. Highly reflecting, uniform and adherent HGS thin films with faint black colour were obtained. The structural, optical and surface morphological properties of the HGS films were investigated. [28-30]. [32-34].

Experimental Method

Commercial glass substrates were degreased in sulfuric acid (H_2SO_4) for 30 min and then immersed in isopropanol ultrasonically for 20 min. Finally, they have cleaned again ultrasonically with distilled water for 10 min and dried in air. The composite HGS thin films were deposited on this glass substrate using chemical bath deposition (CBD) technique in an alkaline medium. The AR grade HgCl_2 , CrO_3 and $\text{NH}_2\text{-CS-NH}_2$ are the initial precursors are used. In the procedure; 10mL (0.1M) solution of HgCl_2 was taken in a 100mL beaker and 20mL (0.1 M) chromic oxide (Cr_2O_3) was mixed in it. For a fabrication of the complex, 10mL (0.1 M) Na_2EDTA (ethylene-diamine-tetra-acetic acid) was added into the mixture of HgCl_2 and Cr_2O_3 . By adding drop-wise ammonium hydroxide solution (7%) the pH of resultant solution was adjusted to 10. At the last 30mL (0.1M) solution of thiourea was added into the above-mentioned mixture. The slow-release metal and chalcogenide ions in the solution condense onto the substrates resulting in thin film formation. The glass beaker containing resultant solution was kept in an oil bath at 65°C for two hours. Finally, deposited samples were taken out of the solution, cleaned with distilled water and dried in air. The prepared thin films were preserved in an air-tight container for further characterization. The so deposited composite HGS films exhibits black yellowish colour. After deposition time, the glass substrates with composite HGS films were removed from the bath and washed with doubly distilled water, dried in air and preserved in an airtight plastic container for further characterization. To obtain good quality films, the amount of complexing agent, the deposition time, temperature, concentration of reactants and pH of the solution were optimized.

Characterization techniques

The thickness of the HGS films was determined by weight difference method using a sensitive microbalance. Structural analysis of the films was carried out using Rigaku (D. Max. C X-ray diffractometer and Ni filter). UV-Visible absorption analysis was done using UV-Vis-NIR spectrophotometer (Jasco-V 570). SEM measurements were carried out with a 250 MK⁻³ Cambridge stereoscan, operated at 15 kV. The optical absorption studies were carried out using Systronic spectrophotometer in the wavelength range 350– 850 nm. To study the electrical characteristics of the films, resistivity measurements were carried out using dc Four-probe method in the temperature range 300–500 K. The type of electrical conductivity was determined from thermoemf measurements.

Results and Discussion: -

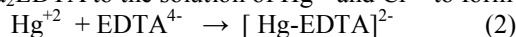
Reaction Mechanism

The chemical bath process mechanism performed by slow release of S²⁻ and controlled free ions of Hg²⁺ and Cr³⁺ react with each other to get HGS nuclei product on glass substrate in the form of precipitated material. EDTA is an amino-derived organic-compound known to be a strong hexadentate chelating agent [35]. It affects the adsorption and desorption processes [36] also forms a complex with metal ions and dissociates reversibly at a low rate. The chemical reaction for the formation of composite Hg_xCr_{2-x}S₄ (x = 0.6) by CBD is given by -

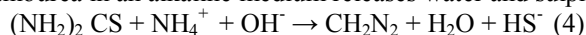
In an aqueous solution, Na₂EDTA finally dissociates as-



By dropwise addition of Na₂EDTA to the solution of Hg²⁺ and Cr³⁺ to form a complex as

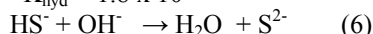


By reaction of thiourea in an alkaline medium releases water and sulphide ions as

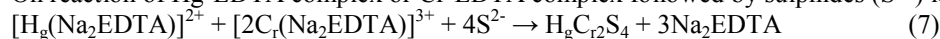


On hydrolysis of ammonia [30], $\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$, (5)

$$K_{\text{hyd}} = 1.8 \times 10^{-5}$$



On reaction of Hg-EDTA complex or Cr-EDTA complex followed by sulphides (S²⁻) ions to forms HGS



[The solubility product $K_{\text{sp}} = 2 \times 10^{-55}$]

The reaction (2), (3) and (6) releases the Hg²⁺, Cr³⁺ and S²⁻ ions and they condense ion-by-ion on the surface of substrate to form HGS thin films.

Characterization using XRD

The X-ray diffractogram for the as-grown Hg_xCr_{2-x}S₄ (x = 0.6) thin film samples were obtained in the 2θ range from 20° to 80°. The X-ray diffraction (XRD) pattern of the films shows crystalline nature with planes having cubic orientations with growth along (2 2 0) plane (JCPDS Card no. 03-065-7116). The use of complexing agents is very common in the preparation of thin films through CBD process. It is very clear that the quality of thin films depends on the nature of the complexing agent. In the XRD pattern (Fig.1.) very few peaks (three) could be detected; for the HGS thin films deposited in the presence of ammonia and ethylenediaminetetraacetic acid (EDTA) as the complexing agent [36]. The deposition time also affects the detection of peaks. The XRD data is given in table-1. The grain size in the film is estimated using Debye-Scherrer's formula.

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

Where β is full width at half maximum (FWHM) in radians, λ is wavelength of the X-ray and θ is the Bragg's angle. The HGS films crystallizes in the normal cubic spinel structure with the space group mF-d3 (No. 227). The value of lattice constant found to be a = b = c = 10.23800 Å. The average grain size for x = 0.6 is found to be 173 nm.

Table- I: Comparison of observed d values with standard d values of HGS thin films.

Planes (h k l)	2 Theta (degree)		d-spacing values d (Å)	
	Standard	Observed	Standard	Observed
2 2 0	24.570	24.560	3.6200	3.6260
4 2 2	43.251	43.160	2.0900	2.0898
5 3 1	52.843	52.840	1.7310	1.7305

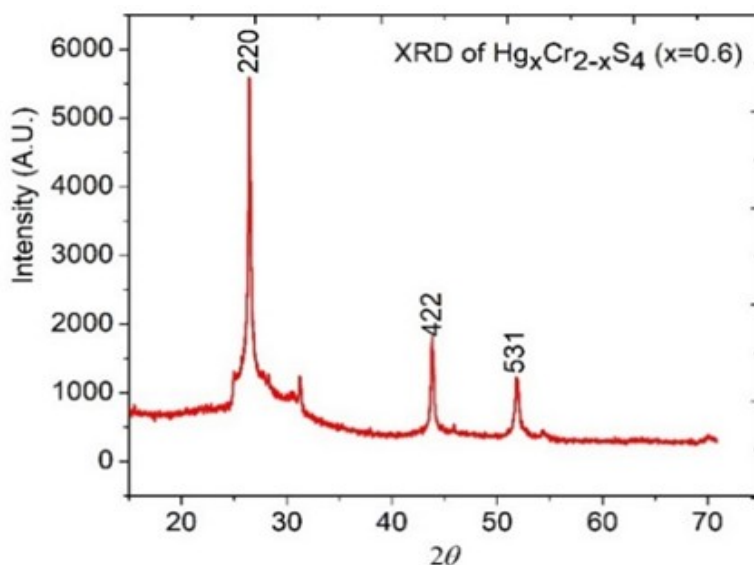


Fig. 1:- XRD pattern for $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) thin film.

Characterization using SEM

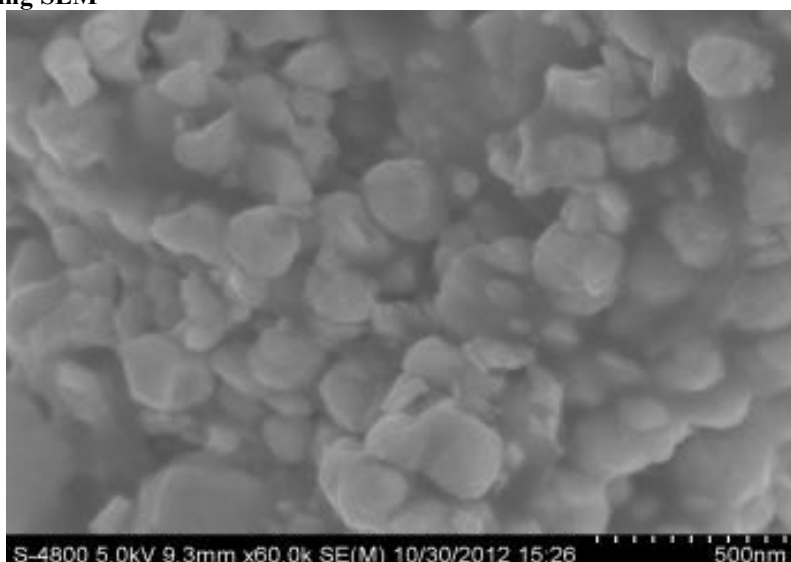


Fig. 2:- SEM image for $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$).

The effect of Cr^{3+} ion in thin film $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) can be studied by SEM. The SEM micrograph of deposited samples is shown in figure 2. The SEM image showed that surface is not smooth and grains are appeared spherical shaped. The grown $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) appears to be porous fibrous group of regularly arranged matrix over which regular fine particles spread with some voids. The grain size of material of films using Cottrell method [37] was found to be in the range 160-170 nm. The surface roughness increased with addition of Cr^{3+} ion.

Characterization using UV-Vis spectrophotometer

Figure 3 depicts the optical absorption spectra of the $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) thin film. At the low optical energy; absorption is minimum and increases with increase in energy. Figure shows the variation of absorbance (αt) with incident photon wavelength. The figure shows that absorption decreases with increasing wavelength also red shift of optical absorption edge. The data were analysed from the following classical relation for near edge optical absorption in semiconductors [38]:

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

Where A is a constant and $n = 2$ for indirect band gap and $n = \frac{1}{2}$ for direct band gap. The plots of $(\alpha h\nu)^2$ versus $h\nu$ of the HGS films shown in Fig. 4. Since the plots of $(\alpha h\nu)^2$ versus $h\nu$ are almost linear, the direct nature of the optical transition in HGS film is confirmed. Extrapolation of these curves to zero absorption coefficient gave the optical energy gap as 2.4 eV which is in good agreement with the values reported by other researchers [39-40]. The decrease in band gap energy value with increase of thickness is commonly observed phenomenon in semiconducting thin films.

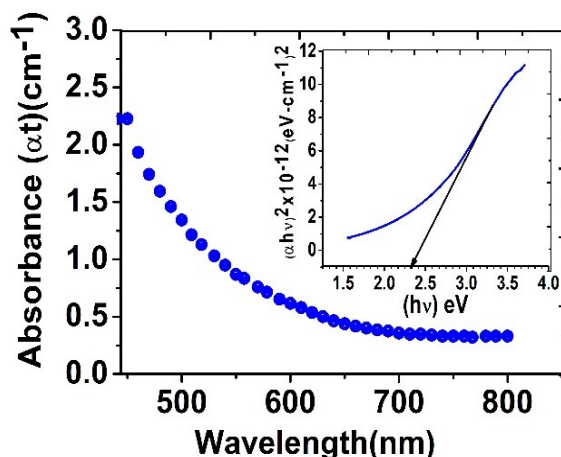


Fig.3:- The variation of absorbance (αt) with incident photon wavelength λ . Fig.4. (Inset figure) Plots of $(\alpha h\nu)^2$ $h\nu$ thin films deposited on glass substrate.

Electrical properties

Electrical resistivity

The two-point dc probe method of dark electrical resistivity measurement was used to study the variation of electrical resistivity with temperature. The variation of $\log \rho$ with reciprocal temperature (K^{-1}) is depicted in Fig. 5. It is observed that the resistivity of film was decreased with increase in temperature, indicating a semiconducting electrical behaviour. The electrical resistivity depends on the structure of the films and working temperature. An increase in temperature affects the structure of films due to increase of grain size and removal of defects on the surface of films. The electrical resistivity of $Hg_xCr_{2-x}S_4$ ($x = 0.6$) was measured in the temperature range 303⁰K to 423⁰K and was observed to be $1.3703 \times 10^3 \Omega\text{-cm}$ to $2.1243 \times 10^3 \Omega\text{-cm}$ [40]. The plot of $\log(\rho)$ Vs ' $1000/T$ ' is almost straight line, indicating that conduction in the film is through thermally activated process. The activation energies were calculated using the relation:

$$\rho = \rho_0 e^{\frac{E_a}{kT}} \quad (10)$$

where ρ is the resistivity at temperature T, ρ_0 a constant, K the Boltzmann constant, T the absolute temperature and E_a the activation energy. The activation energy represents the location of trap levels below the conduction band. The slope of the straight line gives information about activation energy and is observed to be 0.254 eV for low temperature regime and 0.542 eV for high temperature regime.

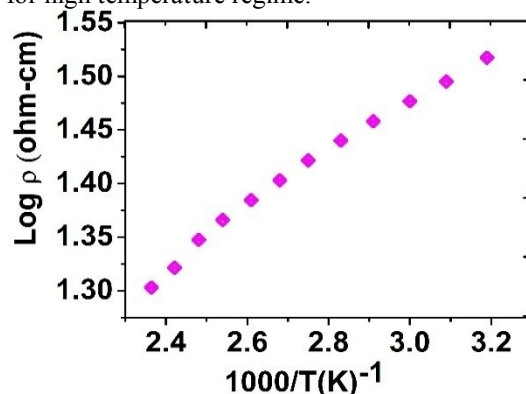


Fig. 4:- Variation of dark electrical resistivity ($\log \rho$) with reciprocal temperature ($1000/T$) of $Hg_xCr_{2-x}S_4$ ($x = 0.6$) thin film deposited on glass substrate.

Thermoemf measurement

In the thermoemf measurement the temperature difference causes the transport of carriers from the hot end to the cold end and thus creates an electric field, which gives the thermal voltage. This thermally generated voltage is directly proportional to the temperature difference created across the semiconductor. The polarity of the induced emf for $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) film indicates an n-type electrical conductivity.

Conclusions:-

A chemical bath deposition method was used in the deposition of $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) films. The X-ray diffraction studies showed that the compositions of the deposited films correspond to $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$). X-ray diffraction study reveals crystalline nature with cubic structure of the film. From electrical resistivity data, it is clear that the films were semiconducting in nature. The $\text{Hg}_x\text{Cr}_{2-x}\text{S}_4$ ($x = 0.6$) films exhibited direct band gap transition with band gap energy of 2.4 eV. The n-type conductivity of these materials was confirmed from TEP measurements.

The study of optical Properties that present composition may be used in the application of p-n junction formation, solar cell design and photovoltaic applications. An increase in electrical resistivity with increasing temperature is attributed to the removal of defects on the surface of films.

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