

Structural and Optical Properties of Chemically Deposited La,Ho Doped Ag₂S Films

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ABSTRACT

The (Ag₂S):cdcl₂,Pr,Ho thin films have been prepared by chemically bath deposition technique at room temperature. The outcomes of Scanning electron microscopy (SEM), photoluminescence (PL) emission spectra and photoconductivity (PC) rise and decay studies are reported in the prepared samples. The SEM Micrograph show void ball-type structures and its group's together forms layer, some flower type structure are also observed in doped films. The optical absorption spectra show the presence of Pr, Ho in the lattice. In the Photoconductivity rise and decay studies the effect of flux, impurities and photo to dark current ratio I_{pc}/I_{dc} is observed. The value of $I_{pc}/I_{dc} \sim 10^4$ is obtained for the host and impurity doped films. In the photoluminescence (PL) study we have observed Excitation and Emission peaks are related to transitions between excitonic levels and levels due to Pr, Ho.

Keywords : PC, PL, SEM, Ag₂S

I. INTRODUCTION

In the last few years, there is a growing interest in silver sulphide films because of their unique electrical (dhumure.et al., 1994, Sankpal.et al., 2000), optical (Ezenwa.et al., 2012), photovoltaic (Nasrallah.et al., 2005) and thermoelectric properties (Muhoz.et.al., 1997, Brelle.et.al.,1998). These unique properties suggest potentially broad applications of silver sulphide films in various devices such as solar cells, super ionic conductors and semiconductors, photo detectors, photo thermal conversion, electro conductive electrodes, microwave shielding coating etc (Krylova.et.al.,2012). Compared to other metals, silver (Ag) and copper (Cu) thin films possess very low specific bulk resistivity of $1.59\mu\Omega\text{cm}$ and $1.68\mu\Omega\text{cm}$, respectively (Adams.et.al. 2008) and therefore silver (Ag) and copper (Cu) are intensively used in ULSI metallization technology.

The Photoconductivity and photoluminescence studies of Silver sulphide type materials are quit important because of their wide technological applications. Silver sulphide (Ag₂S) is an important chalcogenide compound which has been investigated for its numerous applications. Silver sulphide (Ag₂S) belongs to I-VI compound semiconductor materials with monoclinic crystal structure. This dense black solid constitutes the tarnish that forms over time on silver ware and other silver objects. Silver sulphide is insoluble in all solvent but is degraded by strong acids. This material has three forms, known as monoclinic, body- centered cubic and face centered cubic forms. The structure of Ag₂S is orthogonal. It is found in nature as relatively low temperature acanthine. Acanthine is an important ore of silver. (Ezenwa.et.al.2012). The Chemical bath deposition method is relatively simple, inexpensive and highly reproducible technique. In the past decade silver sulphide thin film by CBD method have been

successfully prepared on silica (Mane.et.al.,2000) glass (Okoli.et.al.,2010) and polyamide surfaces(Gotoh.et.al.,2003). There are number of techniques like sol-gel electrostatic deposition, solvent growth d.c.magnetron, sputtering ,molecular beam epitaxy , PVP assisted solvo-thermal method , self-catalytic growth, hydrothermal synthesis , and chemical bath deposition etc. Were used for the preparation of various semiconducting materials and nanocrystalline materials. By CBD method, the dimensions of the crystallites can be varied controlling deposition parameters like reaction time, temperature, ph, and presence of impurities in the solution. CBD is a method of growing thin film of certain materials on a substrate immersed in an aqueous bath containing appropriate reagents at temperatures ranging from room temperature to 373K.Therefore it is planned to prepared films by CBD technique using appropriate fluxes and impurities and complexing agents to control reaction rate and hence to investigate the corresponding changes in structural and optical properties.

II. EXPERIMENTAL DETAILS

The films were grown on substrates of microscopic glass slides in an solution of Silver nitrate, thiourea, ammonia and distilled water. The glass slides were cleaned with acetone and distilled water. The glass slides were dipped vertically into a mixture of solutions of 0.01M silver nitrate, 0.01M thiourea, ethylenediaminetetraacetate (EDTA) and 30% aqueous ammonia. All the chemicals used were of AR grade. All the solutions were prepared in double distilled water. For making the doped films, the 0.01 M solutions of CdCl_2 and Pr_2O_3 , HO_2O_3 were added to the original mixture. After the depositions, the films were cleaned by flushing with distilled water and then dried by keeping the samples in open atmosphere at room temperature. EDTA is used for complexing agent and ammonia solution was used to adjust ph of the reaction mixture and to increase film adherence. For obtaining the good quality of films, time, temperature of deposition and ph of the solution mixture were optimized.

For Photoconductivity rise and decay curve formed the coplanar electrodes on the prepared thin film at a separation of 1mm by applying colloidal silver paint. The photocurrents can be obtained by exposing the total area of the prepared film. For Photoconductivity rise and decay study the light source is 100Watts commercial bulb were used. The photocurrents measurements were done by using a nanometer and for the measurement of voltages, a digital millimeter was used. The Photoluminescence excitation was done by 365 nm line of Hg which was obtained from a high pressure mercury vapour lamp filtered by Carl Zeiss interference filter. Light output was detected by an RCA 6217 photomultiplier tube which was operated by a highly regulated power supply (NIT Raipur).The integrated light output in the form of current was recorded by a sensitive polyflex galvanometer. SEM studies were performed at NIT Raipur using Rigaku scanning electron microscope equipped with Link EDS respectively.

III. RESULTS AND DISCUSSION

Figure 1 (a) and 1(b) shows the SEM micrograph of Ag_2S and $\text{Ag}_2\text{S}:\text{CdCl}_2$. Such micrograph consists of large number of void ball grain particles like structure along with some leafy type of structure. The voids are increases in films of higher CdCl_2 concentration. The SEM micrograph of $\text{Ag}_2\text{S}:\text{Pr}$ and $\text{Ag}_2\text{S}:\text{Ho}$ films are shown in figure 1(c) and 1(d) respectively. Flower and leafy type structure are observed and it is found that the void ball structure changes rapidly to the well crystalline shapes. The bigger leafy structure in the present case also shows overlap of void ball structures. The presence of Pr and Ho in the material increases the crystalline effect and the micrograph look beautiful groups of white color flower and it can also be seen that the Ho reduce the size of the void ball particle. The dark space present in the micrograph related to absence of matter (Sensors & Transducers).The scattered leafy structure may also be expected when overlap does

not take place .Presence of voids also seen in such growth. Photoluminescence (PL) Study Table 1.

Table 1

Samples	Peaks position(nm)	Intensities(a.u.)
Ag ₂ S	351.23 578.65	655 1030
Ag ₂ S:cdcl ₂	298.21 400.11 588.07	455 155 1001
Ag ₂ S:Pr	320.34 416.41 590.62	885 101 1020
Ag ₂ S:Ho	301.13 408.72 602.02	911 56 1015

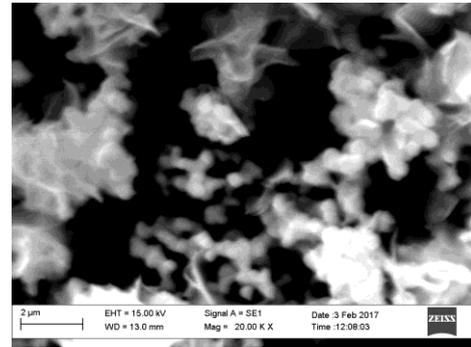


Figure 1(c)

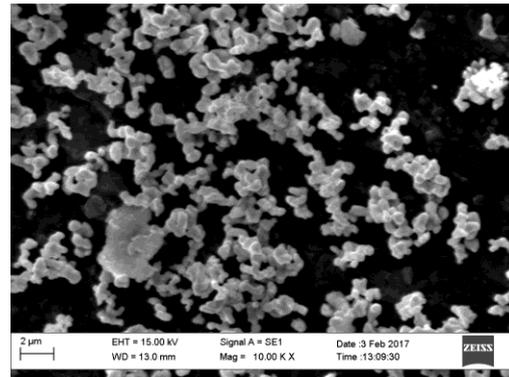


Figure 1(d)

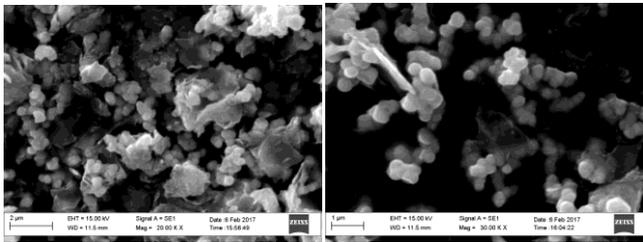
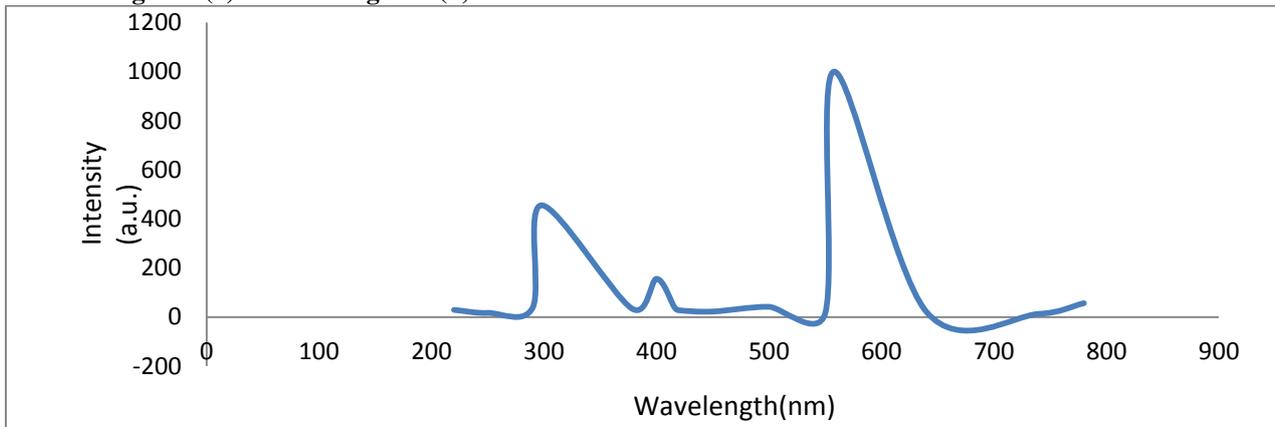


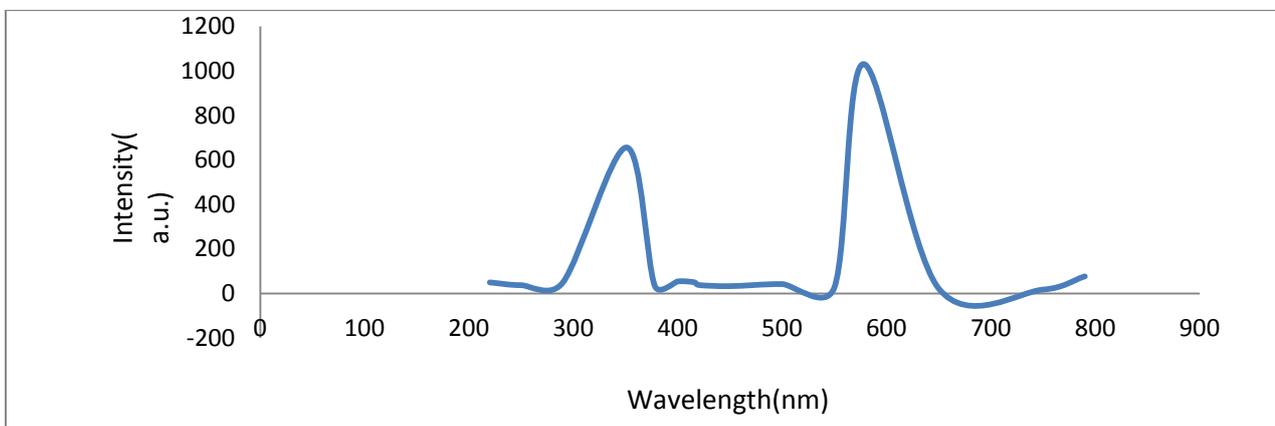
Figure 1(a)

Figure 1(b)

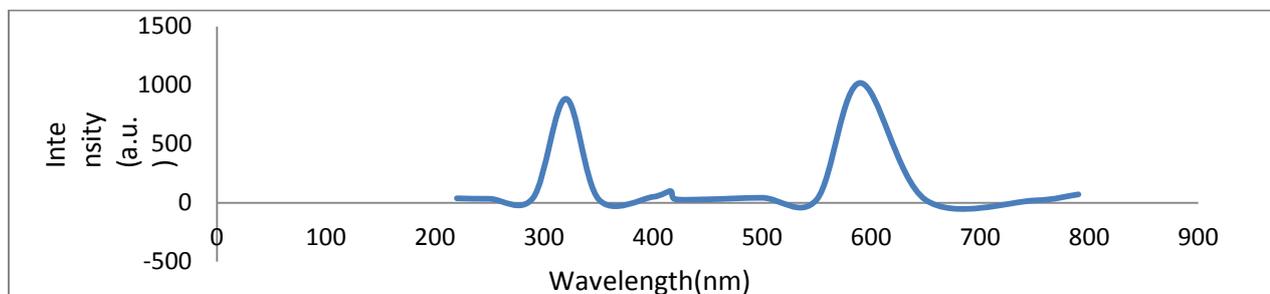
Figure 1. The SEM micrograph of (a) Ag₂S film (b) Ag₂S:cdcl₂ film (c) Ag₂S: Pr (d) Ag₂S:Ho



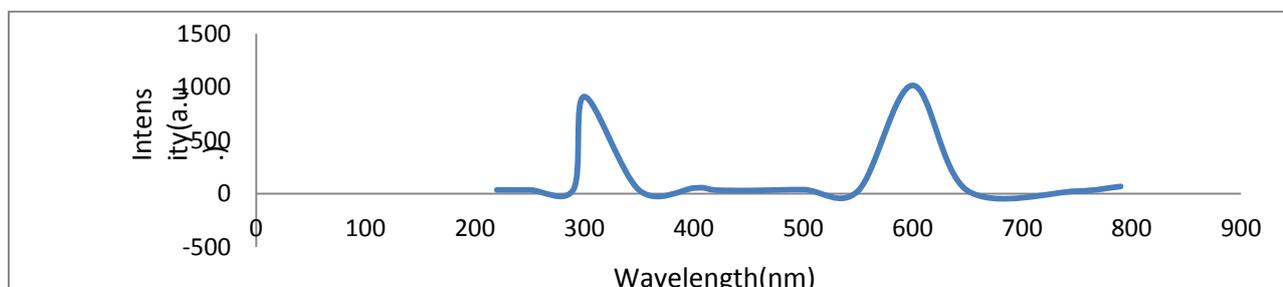
Gharp 1(a)



Gharp 1(b). Ag₂S:cdcl₂



Gharp 1(c). Ag₂S:Pr



Gharp 1(d). Ag₂S:Ho

Figure 2 PL Spectra of Various Ag₂S films

The PL Spectra of various nanocrystalline Ag₂S films are presented in Figures 2. The emission spectra were recorded under 220nm excitation wavelength. The Value of Wavelength and Intensities are listed in table 2. A strong Peaks Centered at 578.65nm and a weak peak at 351.23nm. This shows that the shift in emission peak to the lower wavelength side. 578.65nm peaks correspond to band to band transition due to blue shift of emission of Ag₂S and also correspond to increased band gap of Ag₂S. In addition of cdcl₂ the enhancement of Intensity of PL emission and a small peak position observed. The spectra show emission peak at 400.11nm along with broadening of the other peak at 588.07nm. The improvement of intensity due to energy transfer from flux level.

Doping of La and Ho as impurity in Ag₂S films resulted in an enhancement of intensity of PL emission. In the PL spectra of Pr doped film three peaks are observed. Two peaks correspond to the 320.34nm and 416.41nm and one peak related to 590.62nm. In the presence of Pr there is a change in intensity of the third peaks. The emission expected from the transitions between energy levels of Pr are 295nm(S-G), 335nm(S-D) and 335nm(S-I). In the

present study the peaks are not exactly same as the observed peaks but the intensities are affected. This confirms that the energy transfer takes place from Pr to the levels of Ag₂S. In case of Ho doped films we have found three peaks similar to the Pr doped case but the wavelength are different and also the intensities are different 301.13nm, 408.72nm and 602.02nm are observed. It is clearly showed that incorporation of Ho the change in intensities is seen. In both the cases (Pr and Ho doped) one small peaks are present and their wavelength are nearly the edge of visible region. That is the conformation that the emission is in the visible region.

Photoconductivity study

The rise and decay curves of different Ag₂S film are shown in figure 3. Quite good photocurrent was found in the prepared samples. In presence of cdcl₂, Ho, Pr the photocurrent is increases. Earlier worker found the role of cdcl₂ as improving crystallinity and as flux in present case it is found correct. Showing maximum photocurrent at a particular concentration shows that probably excess Cd may be incorporated in the lattices which help in increase in photocurrent. After a particular concentration, concentration quenching may take place.

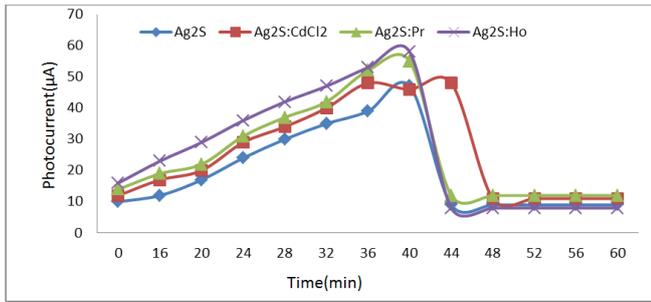


Figure 3. Photoconductivity curve of Various Ag₂S films

The formation of electron-hole pair take place if the radiation falls on the thin films prepared by the chemical bath deposition (CBD) method. This electron hole pair (photo carriers) becomes responsible for the photocurrent observed in the samples. In the Photoconductivity curves fast rise in the beginning followed by saturation. It is observed that the increasing part of the curve is due to the generation of photo carries. The slowly increasing part of the photocurrent is occurs because of recombination comes into pictures and dominant in this part. It is clear that the decay rates slower in both the case of Pr and Ho doped films. The Exponential equation can be used for the mathematical analysis of the decay part. The ratio of photocurrent (I_{pc}) to dark current (I_{dc}) is observed and the order is found to be 10^4 which is quite good

The corresponding values of I_{pc} , I_{dc} , gain, τ (life time), μ (mobility) and trap depth are listed in table 2. The generation of photocurrent increases when the $cdcl_2$, Pr and Ho incorporated in the host material Ag₂S, so more charge carries generated by the flux and the rare earth element. It is observed that the role of rare earth element and Flux is to generate the platform of the charge carries to come in the conduction band and gives the conductivity.

IV. CONCLUSION

The undoped and doped Ag₂S films show good Photoconductivity properties. In the present work undoped and doped Ag₂S films have been successfully prepared by chemical bath deposition

method using Silver nitrate, ammonia-thiourea system. The SEM micrograph shows Flower and leafy type structure and it is found that the void ball structure changes rapidly to the well crystalline shapes. PL spectra show that in presence of $cdcl_2$, Pr and Ho the emission peaks observed in visible region. The Photoconductivity studies of prepared thin films reflect information that the generation of photocurrent is very fast and decay rates appeared to be slower. The photoconductivity gain is in the order of 10^4 . So it is found that the doped and undoped Ag₂S films prepared by CBD technique are found to be good photosensitive and photovoltaic material.

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