

STRUCTURAL AND OPTICAL PROPERTIES OF Ho, Pr DOPED RARE EARTH ELEMENT IN Ag₂S THIN FILM OBTAIN BY CHEMICAL BATH DEPOSITION TECHNIQUE

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The Ho,Pr doped silver sulphide thin film have been prepared by chemically bath deposition technique at room temperature. The semiconducting films were grown in bath containing aqueous solution of silver nitrate, thiourea, EDTA, ammonia and used the Pr, Ho as the Rare Earth element. Silver nitrate used for the silver ion source, thiourea for sulphur ion source, EDTA is the complexing agent and ammonia for pH. The SEM Studies of doped Pr silver sulphide films show the void ball type structure and it is grouped together and look like the granular bunch of solid material along with existence of micro particle and for the Ho doped film flower and leaf type of structure are found. In The FTIR spectrum of prepared sample the peaks of vibration appear located at 400-600 cm⁻¹ in all the entire film and N-H, C-O, O-H bonding present in the plotted curve. In the Photoluminescence study the emission peaks fall around 560nm to 600nm wavelength and Excitation peak found 300nm to 332 nm of the prepared films. High transmittance, low reflectance found in the visible region in the entire prepared sample. The absorption peaks fall on the UV region. High Photocurrent is found, and in dark current study the linear behavior between voltage and current are seen. The photoconductivity rise and decay curve have also plot and found that it is similar to the reported curve. In the excitation spectra photocurrent exist in the ultra violet region. Quite good photosensitivity material is observed in Pr, Ho doped silver sulphide films.

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1. Introduction

Metal chalcogenide semiconducting thin films have received much attention due to their world-wide applications in various fields of science and technology (3). 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 mono-clinic, 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 (5).

In the last few years, there is a growing interest in silver sulphide films because of their unique electrical (4, 12) optical (5), photovoltaic (10) and thermoelectric properties (9, 2). 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, electroconductive electrodes, microwave shielding coating etc (7). Compared to other metals, silver (Ag) and copper (Cu) thin films possess very low specific bulk resistivity of 1.59μΩcm and 1.68μΩcm, respectively (1) and, therefore are intensively used in ULSI metallization technology.

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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 (8) glass (11) and polyamide surfaces (6). 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.

2. Experimental details

The $\text{Ag}_2\text{S}:\text{Pr}$ and $\text{Ag}_2\text{S}:\text{Ho}$ thin films were grown from a solution of Silver nitrate and thiourea in an alkaline solution of ammonia and distilled water. Glass slides used as substrates were cleaned in distilled Water, HCl and acetone ultrasonically. The glass slides were kept vertically in a Solution prepared by CBD. The deposition of $\text{Ag}_2\text{S}:\text{Pr}$ and $\text{Ag}_2\text{S}:\text{Ho}$ films was done in a chemical bath prepared in a beaker by addition of solutions of 8ml of 0.1 M Silver Nitrate Which is the source of Silver, 25ml ammonia added for the maintaining pH alkaline medium, 8 ml of 0.1 M thiourea Mixed is the source of sulphur and 2ml EDTA used as a complexing agent. The Pr and Ho of 0.001 M are added with different Concentration to the basic Solution of Ag_2S . The Solutions of 0.1M thiourea 0.1M Silver Nitrate, 0.1M cadmium Acetate, 0.001M Pr and 0.001M Ho were prepared from analytical grade chemicals. Film deposition was produced by precipitation followed by condensation on glass substrates. All the thin films were prepared at a room temperature for 5 hour. The resultant prepared films were homogeneous, well adhered to the substrate

3. Result and discussion

3.1. FTIR STUDY

The FTIR spectrum of $\text{Ag}_2\text{S}:\text{Pr}$ and $\text{Ag}_2\text{S}:\text{Ho}$ with different concentration shown in the above figure. The maximum peaks of vibration found around 400-600 cm^{-1} in all the prepared film. The above figures show at the recorded FTIR spectra from 3500 cm^{-1} to 400 cm^{-1} range of the prepared films. In case of $\text{Ag}_2\text{S}:\text{Ho}$ (2ml) fig 1(A) the broad and small peaks observed at 3422.87 cm^{-1} due to N-H stretching vibration, 2924.29 and 2364.62 cm^{-1} due to the aliphatic symmetric and asymmetric C-H stretching, 1735.76 cm^{-1} , 1618.02 cm^{-1} , 1419.99 cm^{-1} correspond to C=O and the peaks correspond to 1030.98 cm^{-1} for O-H bonding. The characteristic vibration of bulk Ag_2S and Pr, Ho rare earth doped silver sulphide falls at the 400-600 cm^{-1} . Small hump found in Fig 1 a), Fig 1c) and Fig.1 f) curve at the 1600 cm^{-1} to 1400 cm^{-1} range which also correspond to C=O bonding stretching and bunch of peaks involve in 650 cm^{-1} to 400 cm^{-1} because of O-H. It is observed that in fig. 1 d) there is a band at 3407.87 cm^{-1} due to N-H stretching vibration while the strong band at 1560.64 cm^{-1} for the C=O. The peaks correspond between 651 cm^{-1} to 400 cm^{-1} due to the presence of moisture. The small hump observed in few case of bulk and doped film because of some moisture in the form of water molecules present in the films.

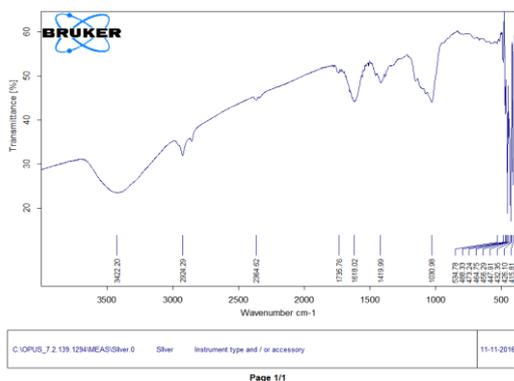


Fig . 1. a) FTIR Spectra of $Ag_2S:Ho(2ml)$

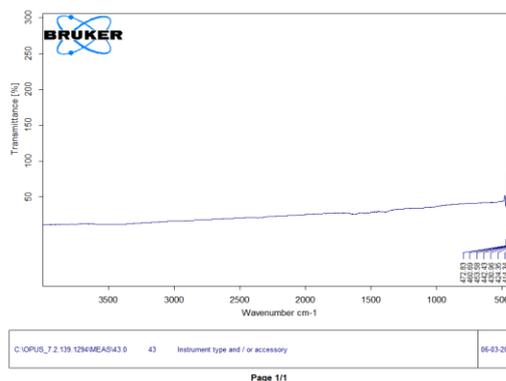


Fig . 1. b) FTIR Spectra of $Ag_2S:Ho(4ml)$

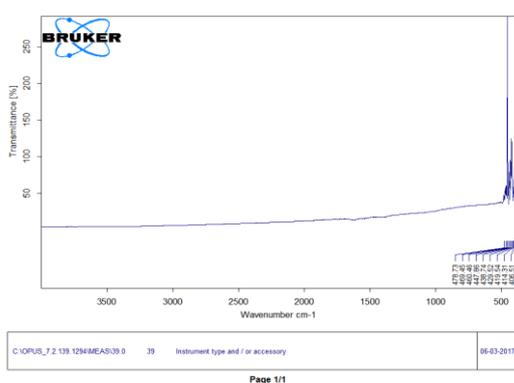


Fig . 1. c) FTIR Spectra of $Ag_2S:Ho(6ml)$

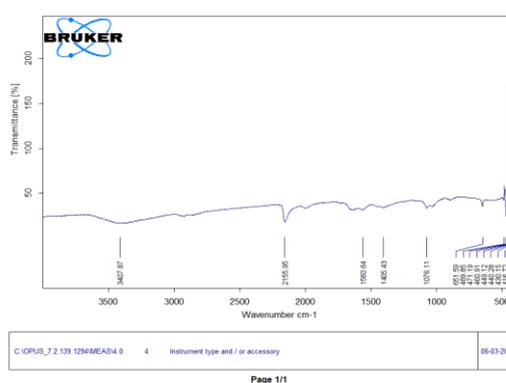


Fig . 1. d) FTIR Spectra of $Ag_2S:Pr(2ml)$

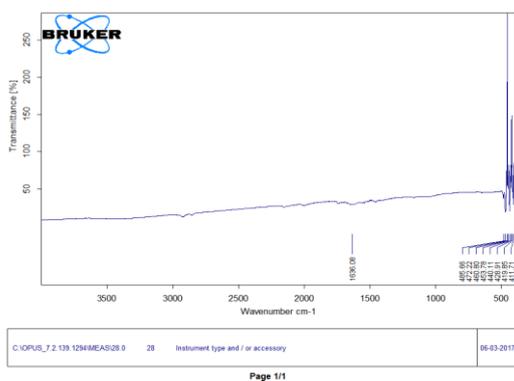


Fig . 1 e) FTIR Spectra of $Ag_2S:Pr(4ml)$

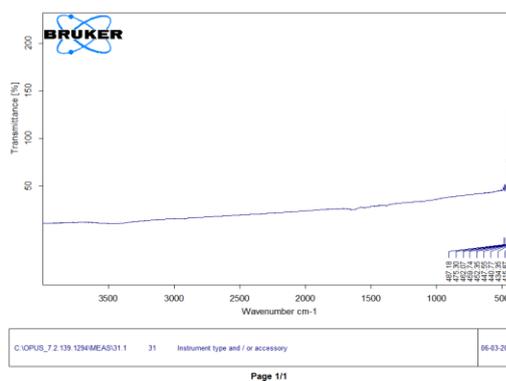


Fig . 1 f) FTIR Spectra of $Ag_2S:Pr(6ml)$

3.2. Photoconductivity study

Dark Current study

The Following Figure 2(a) and 2(b) Show that current will be increases with applied voltage in linear manner of the entire film of $Ag_2S:Pr$ and $Ag_2S:Ho$. So the dark current and applied voltage follows the ohms law. The electrode is formed on the prepared materials and voltmeter and ammeter are connected in series. In the Dark Current Study the prepared materials kept in dark region that means there is no light comes near to the prepared samples. The prepared thin films are good for conductivity. The concept of dark current in the semiconducting thin films is the movement of thermally excited charge carriers inside the material. Some of the charge carriers are jump into the conduction band which is responsible for the conductivity. The dark current appears for limited voltage .We have observed the dark current appears in nano scale

range and also observed that the dark current decreased when Pr and Ho rare earth concentration increases in the Silver sulphide .

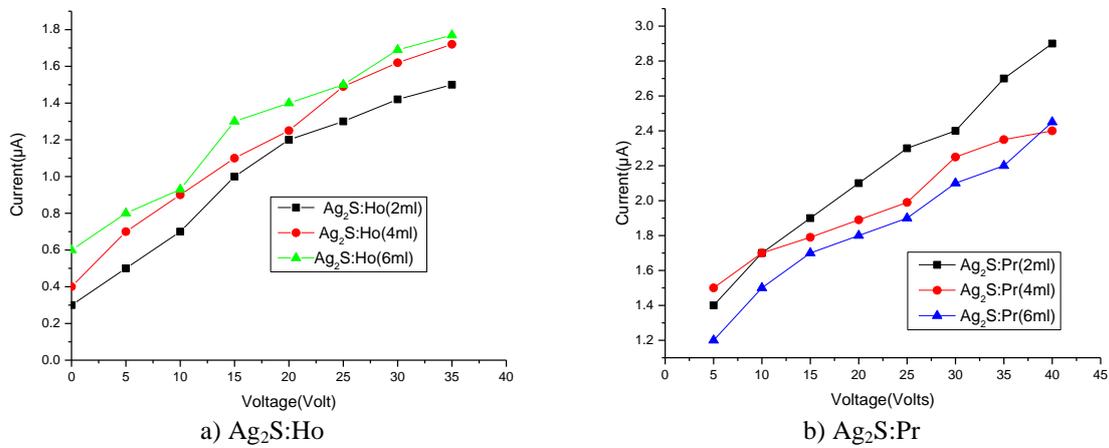


Fig. 2 Plot of dark current vs Voltage of different concentration of Ho

Photocurrent study

The following diagram shows the rise and decay curves for $\text{Ag}_2\text{S}:\text{Pr}$ and $\text{Ag}_2\text{S}:\text{Ho}$, with different concentration. All the films reported here are prepared at room temperature. The deposition time for the films was 5 hour. The rise and decay curve looks similar in the entire sample. When the radiation fall on the prepared thin films material the electron hole pair (photo carriers) becomes originate and those are responsible for the photocurrent. In the Present curves fast rise in the beginning followed by saturation. In The increasing part of the photocurrent is due to the generation of photo carries. The slowly increasing part is when recombination becomes dominant. Decay rates slower in both $\text{Ag}_2\text{S}:\text{Pr}$ and $\text{Ag}_2\text{S}:\text{Ho}$ films. The decay part is in the form of exponential equation. The ratio of photocurrent to dark current is found to be the order of 10^4 which is quite good. It is noted that reported thin film is of n-type due to trapping of photo generated holes at boundaries of the negatively charged gains in Semi crystalline thin films. The mobility of charge carries enhance due to the inter gains barrier height is lowered. The generation of photocurrent increases when the concentration of Pr and Ho increases, so more charge carries generated by the rare earth element. The role of rare earth element is to generate the platform of the charge carries to come in the conduction band to gives the conductivity. In the present study the rare earth Pr and Ho are the prominent material for the silver sulphide. Decay rates appeared to be slower in the reported films.

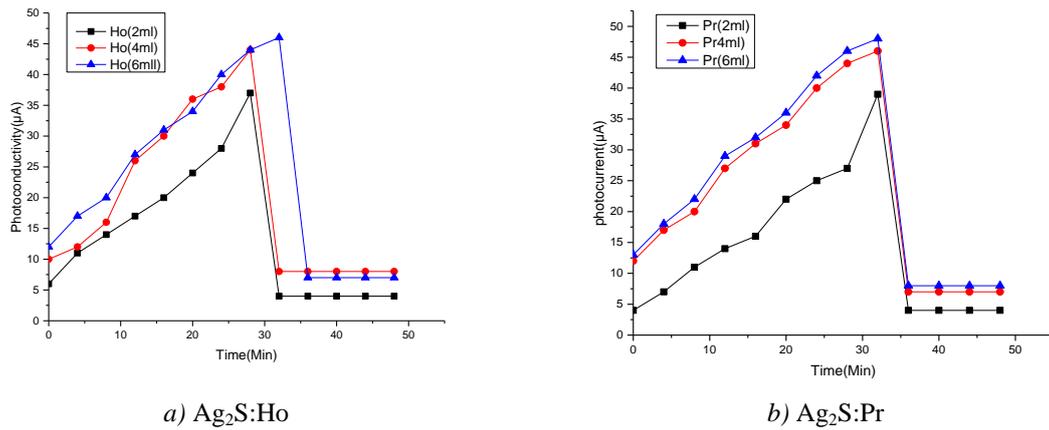


Fig.3 Rise and Decay Curve of Ag_2S with different concentration of Ho,Pr

The lifetime of the charge carries in the steady state can be represented by using the relation

$$\tau = \Delta\tau / \left(\frac{d\sigma}{dt} \right) = \sigma / \tan\delta$$

where σ is the static photocurrent and $\tan\delta$ is the slope of the initial state of the decay curve. The mobility calculated by using the relation

$$G = \tau\mu V/L^2$$

Where G denoted as photoconductivity gain, V is called applied voltage between the electrodes and L is the distance of electrode. The value of E_1 and E_2 called trap depth can be calculated by using the decay law $I_t = I_0 \exp(-Pt)$ where I_t is the photocurrent at the time t after the excitation source is closed, I_0 is the photocurrent at time $t=0$ and P is the probability of escape of an electron from the trap per second. The probability term can be represented by $P = s \exp(-E/kT)$ where s is the frequency factor, E is the trap depth, k is the Boltzmann's constant and T is the absolute temperature. The trap depth can be obtained by following relation

$$E = kT [\ln s - \ln \{ \ln(I_0/I_t) / t \}]$$

Table 1. Value of Dark current, Photocurrent current, Life time, Mobility, Trap Depth and Current gain

Sample	I_{dc} (nA)	I_{pc} (μ A)	Gain $I_{pc}/I_{dc}(x10^3)$	τ (in sec)	μ ($cm^{-1}V^{-1}s^{-1}$)	Trap depths(eV)
$Ag_2S:Ho(2ml)$	1.68	140	76.47	36.21	0.024	$E_1=0.742, E_2=0.725$
$Ag_2S:Ho(4ml)$	1.70	210	125.74	40.29	0.032	$E_1=0.741, E_2=0.730$
$Ag_2S:Ho(6ml)$	1.72	180	93.023	39.12	0.025	$E_1=0.746, E_2=0.728$
$Ag_2S:Pr(2ml)$	1.72	240	134.50	45.25	0.033	$E_1=0.749, E_2=0.741$
$Ag_2S:Pr(4ml)$	1.74	260	122.58	51.10	0.034	$E_1=0.756, E_2=0.748$
$Ag_2S:Pr(6ml)$	1.80	290	188.31	52.52	0.036	$E_1=0.750, E_2=0.742$

3.3. SEM STUDY

The following figure shows the SEM Image of $Ag_2S:Pr$ and $Ag_2S:Ho$ with different concentration. The SEM micrograph of the $Ag_2S:Pr(2ml)$ film clearly show the void ball type structure and it is grouped together and look like the granular bunch of solid material. For the

SEM image of $\text{Ag}_2\text{S}:\text{Pr}(4\text{ml})$ and $\text{Ag}_2\text{S}:\text{Pr}(6\text{ml})$ Ball type structure remain look same in previous concentration bu the size of the ball increases and look as cabbage. In $\text{Ag}_2\text{S}:\text{Ho}(2\text{ml})$ film some crystal and flower tupe structure found.

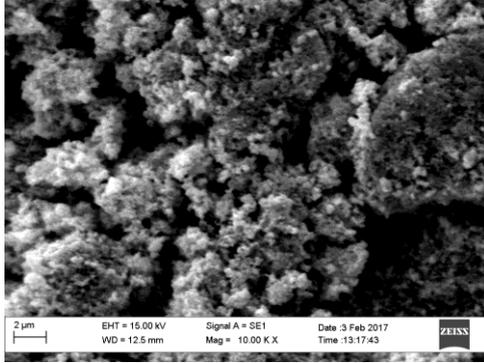


Fig. 4 a) SEM Micrograph of $\text{Ag}_2\text{S}:\text{Pr}$ 2ml

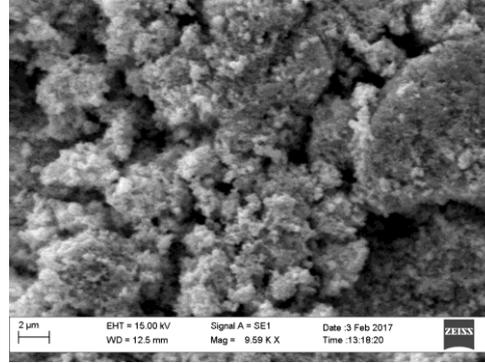


Fig 4 b) SEM Micrograph of $\text{Ag}_2\text{S}:\text{Pr}$ 4ml

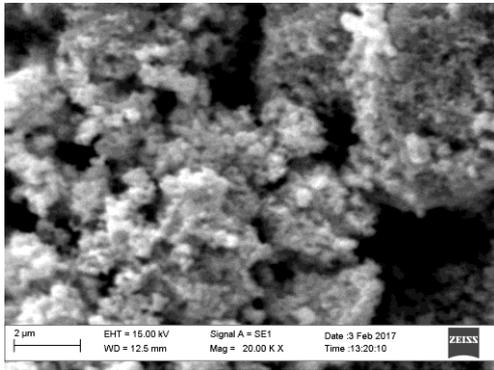


Fig 4 c) SEM Micrograph of $\text{Ag}_2\text{S}:\text{Pr}$ 6ml

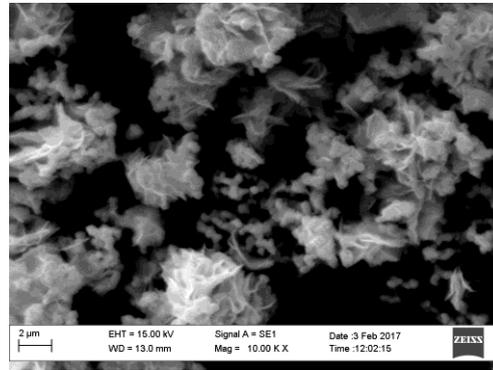


Fig 4 d) SEM Micrograph of $\text{Ag}_2\text{S}:\text{Ho}$ 2ml

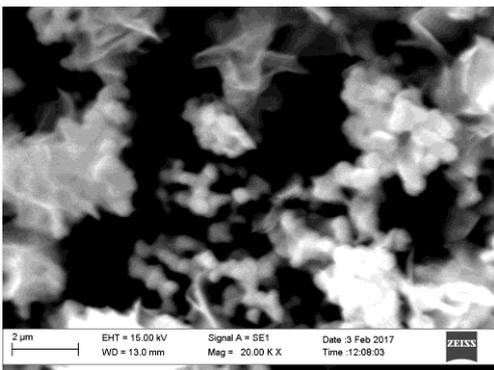


Fig 4 e) SEM Micrograph of $\text{Ag}_2\text{S}:\text{Ho}$ 4ml

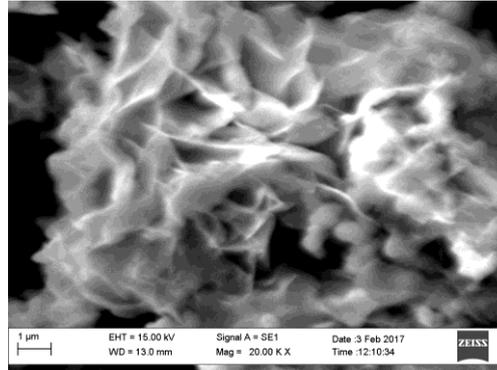


Fig 4 f) SEM Micrograph of $\text{Ag}_2\text{S}:\text{Ho}$ 6ml

The formation of Flower type structure conform that the prepared material are in the definite shape and match the earlier reported article. In case of $\text{Ag}_2\text{S}:\text{Ho}(4\text{ml})$ and $\text{Ag}_2\text{S}:\text{Ho}(6\text{ml})$ the white flower image is clearly show and It is observed that the substrates are well-covered with the deposited layers without cracks and pinholes in the shapes are orthogonal. The presence of Pr and Ho quantized the silver sulphide film to nanocrystalline structure. The SEM micrographs of nanocrystalline $\text{Ag}_2\text{S}:\text{Ho}$ film show more uniform distribution of particles with reduction in voids. The presences of Ho in film are more effective as a result that the Image changes from void Ball

and cabbage structure to the flower type shape. It is found that the doped Ag_2S films are in the nano size structure.

Photoluminescence Study

The Photoluminescence emission and excitation spectra of different concentration of $\text{Ag}_2\text{S}:\text{Pr}$ and $\text{Ag}_2\text{S}:\text{Ho}$ presented in figure 5. The emission peaks were recorded under 560nm to 590nm wavelength in case of $\text{Ag}_2\text{S}:\text{Ho}$ and for the $\text{Ag}_2\text{S}:\text{Pr}$ it is ranging from 550nm to 530nm.

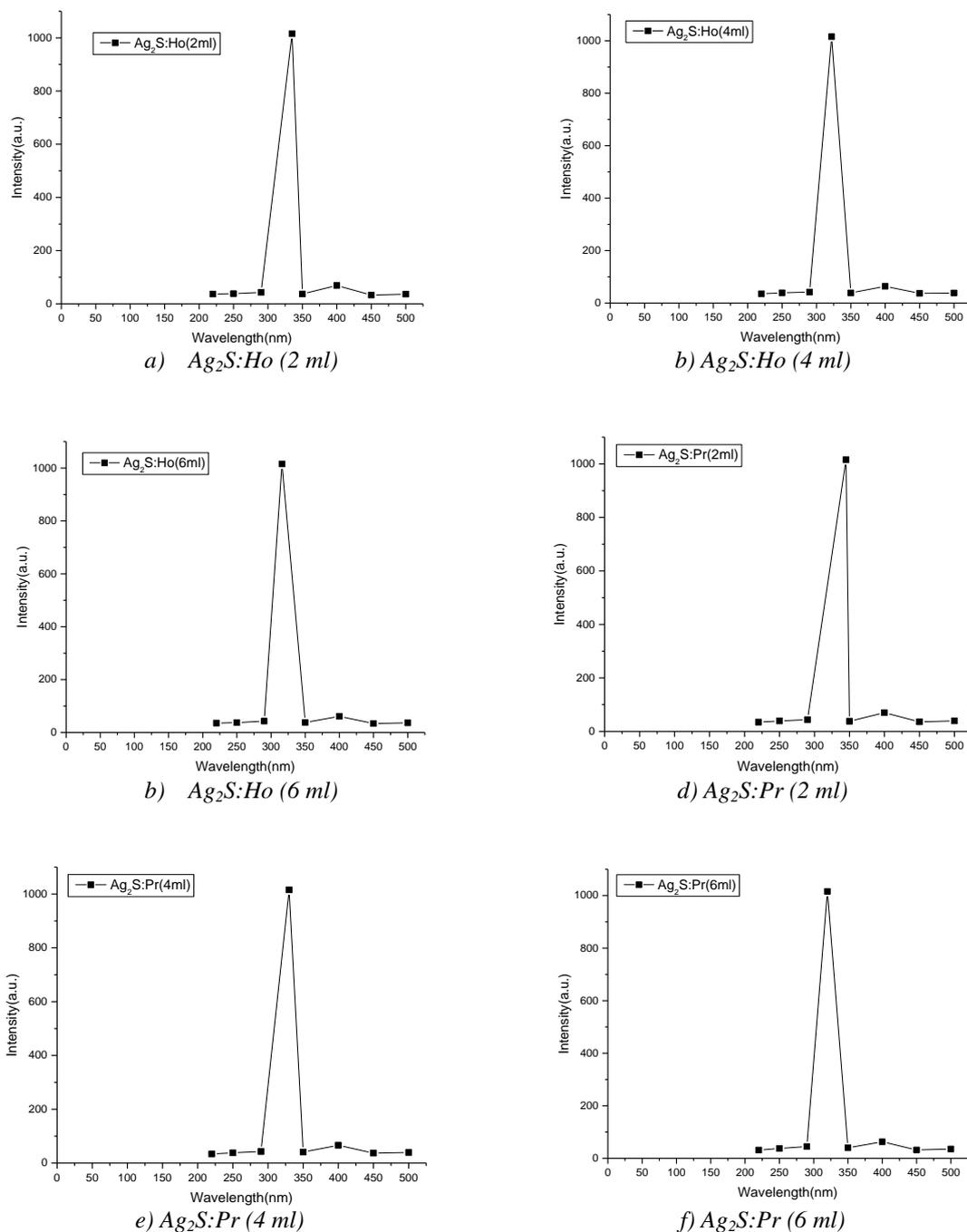


Fig. 5.1 PL excitation curve of Ag_2S with different concentration of Ho, Pr

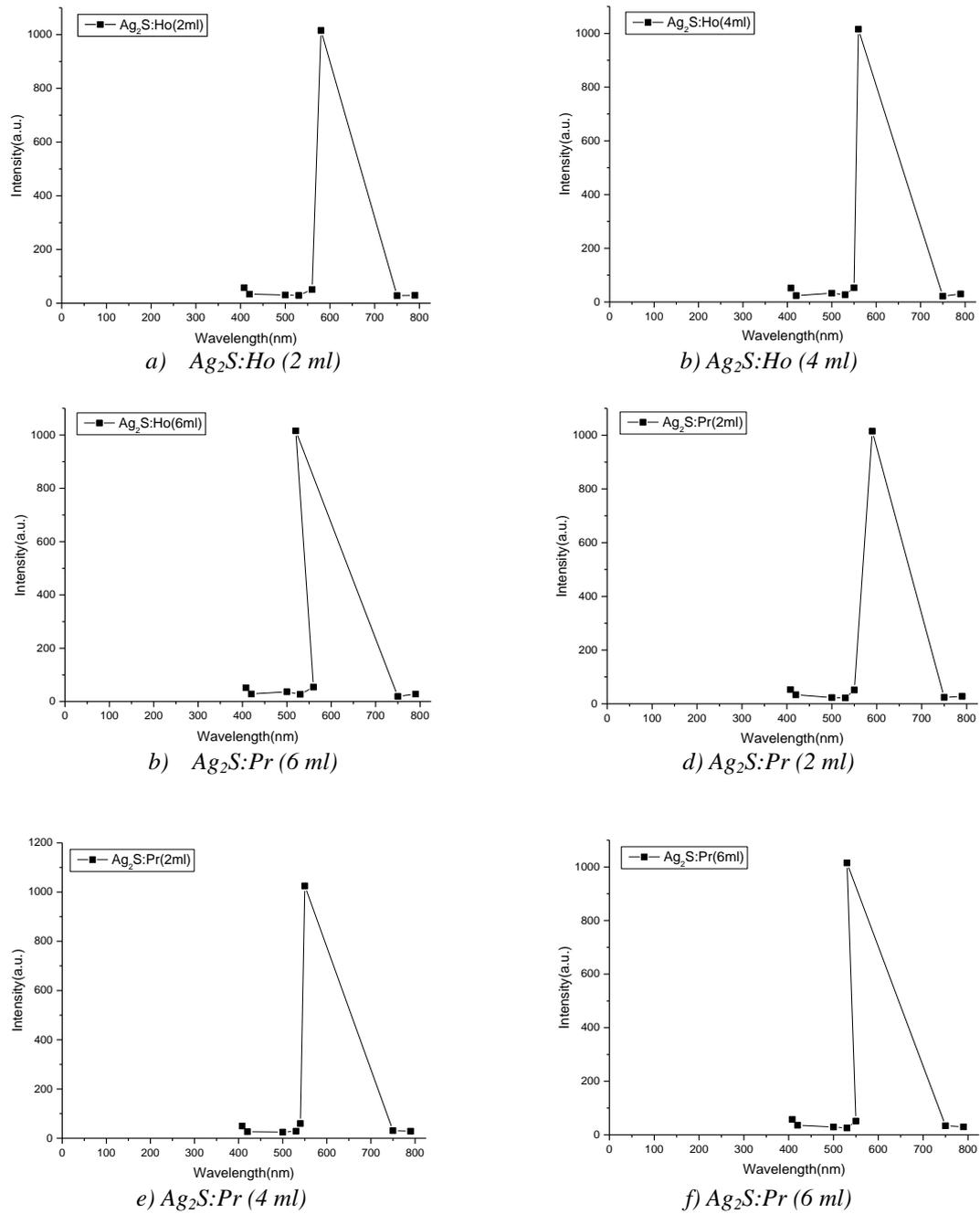


Fig. 5.2 PL emission curve of Ag_2S with different concentration of Ho, Pr

Table 2. Excitation and Emission peaks of prepared sample

Samples	Excitation Peaks	Emission Peaks
$Ag_2S:Ho(2ml)$	335 nm	590nm
$Ag_2S:Ho(4ml)$	322nm	560nm
$Ag_2S:Ho(6ml)$	316nm	560nm
$Ag_2S:Pr(2ml)$	345nm	550nm
$Ag_2S:Pr(4ml)$	330nm	530nm
$Ag_2S:Pr(6ml)$	320nm	520nm

The emission peak will be shifted to the shorter wavelength side in reported thin films. The 590-530nm may be attributed to the band to band transition which occurs due to blue shift of emission of the reported films. We have observed that the excitation spectra peaks found in the range of 345nm to 316 nm of the prepared thin films. In the present study the observed peaks are not exactly same as expected for the transition in this ion however the intensities are surely affected. This shows that the energy transfer takes place from band of Pr to the host emitting centers. The Pr doped silver sulphide is suitable material to absorb Ultra violet radiation and convert it into the visible region.

Study of Excitation Spectra

The studies of excitation Spectral give quite useful information of the prepared films. The shapes of the prepared samples are same. The excitation spectra in which plot of photocurrent in Y axis against wavelength or frequency of the exciting light in the X -axis, gives information about the nature of light near the absorption edge or different from the absorption edge.

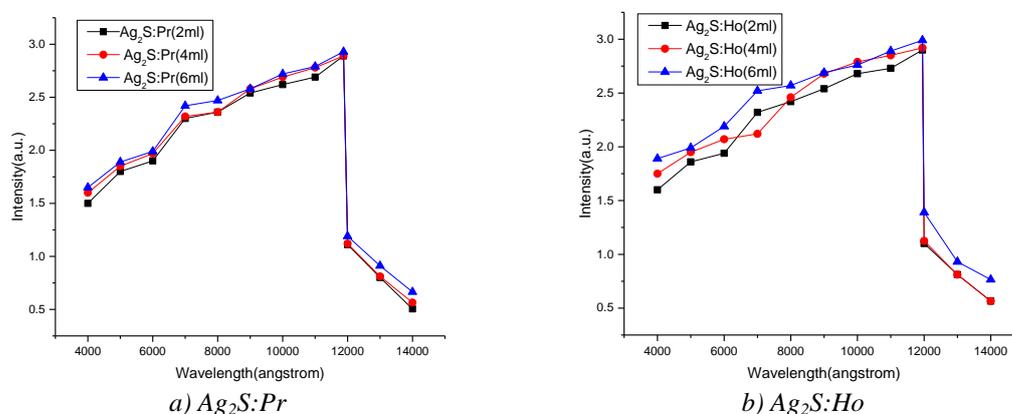


Fig. 6 Excitation Curve of Ag_2S with different concentration of Ho, Pr

The peaks of the excitation spectra are shifted to the higher value of wavelength that indicate the band gap reduce to lower value. The presence of the rare earth element in silver sulphide films the band gaps are decrease that show the quantum confinement occurs in the present work. Fig shows the excitation spectra of different concentration of $Ag_2S:Pr$, and $Ag_2S:Ho$ films. Using the relation $E=h\nu=hc/\lambda$ calculate the corresponding band gap of the reported films.

Table 3. Value of band gap of the prepared sample

Films	Peaks	Band gap
$Ag_2S:Pr$ 2ml	11875Å	1.042eV
$Ag_2S:Pr$ 4ml	11895Å	1.040 eV
$Ag_2S:Pr$ 6ml	11910Å	1.039 eV
$Ag_2S:Ho$ 2ml	11950Å	1.035 eV
$Ag_2S:Ho$ 4ml	12200Å	1.014 eV
$Ag_2S:Ho$ 6ml	12510Å	0.989 eV

3.4. ABSORBANCE STUDY

In the absorbance study of the $Ag_2S:Pr$ and $Ag_2S:Ho$ thin films we have found that the peaks of the curve fall in UV region

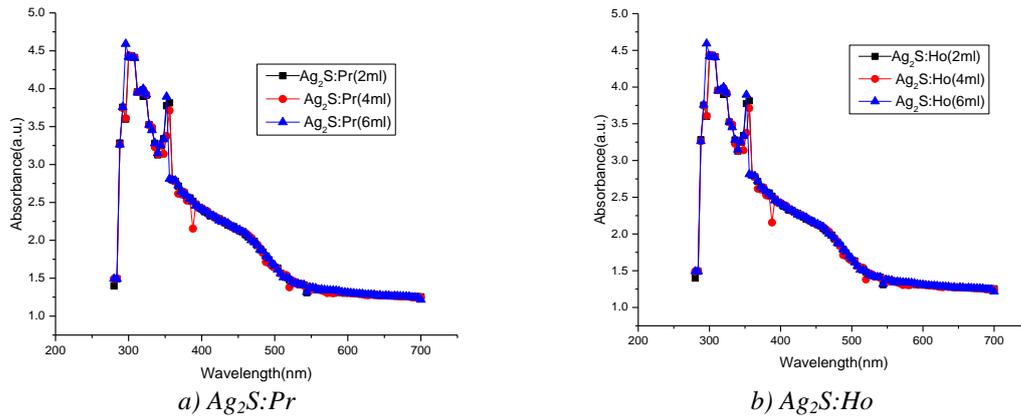


Fig. 7 Absorbance Curve of Ag₂S with different concentration of Ho, Pr

The entire sample gives almost the same absorbance trajectories and it is found that the peaks shifted toward the ending side of UV region, when we have incorporated Pr and Ho element in higher concentration. Almost entire sample falls between 300-370nm wavelengths. From the observation of absorbance study we have found that the reported material is important to use in photovoltaic technology.

3.5. REFLECTANCE STUDY

The following figure shows reflectance curve of different concentration of Ag₂S: Pr and Ag₂S: Ho thin films. Reflectance found to be very low in Ultraviolet, visible and infrared region for the Reported samples. Reflectance is decrease with the increasing wavelength in all the cases. These results reflect information that the silver sulphide material with rare earth element is anti reflection materials.

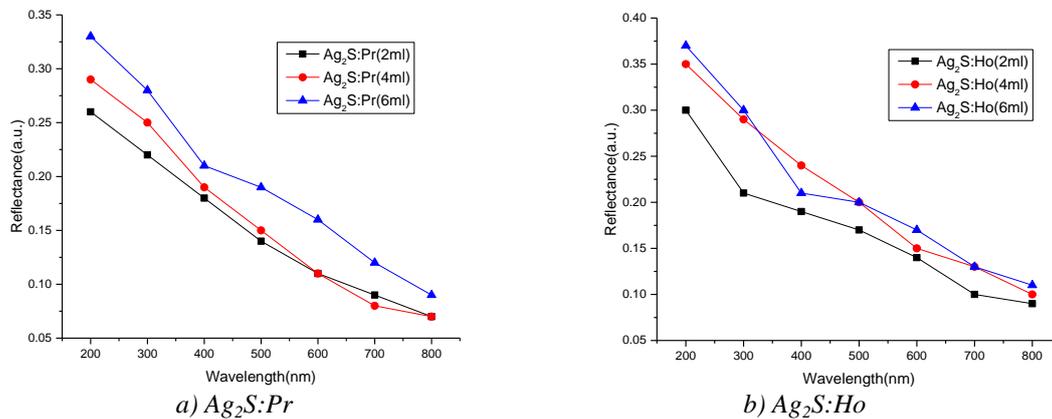


Fig. 8 Reflectance Curve of Ag₂S with different concentration of Ho, Pr

3.6 Transmittance study

The below curves show the properties of transmittance of different concentration of Ag₂S: Pr and Ag₂S: Ho, thin films prepared by chemical bath deposition technique. We have to found that the prepared thin films have low transmittance in the UV regions and it is increase in visible region. From the above curve transmittance had been seen at the 300nm ranging to 800nm. These types of material are very useful for the preparation of the solar cells. It is clear that the silver sulphide thin films are low transmittance and high absorbance in UV regions.

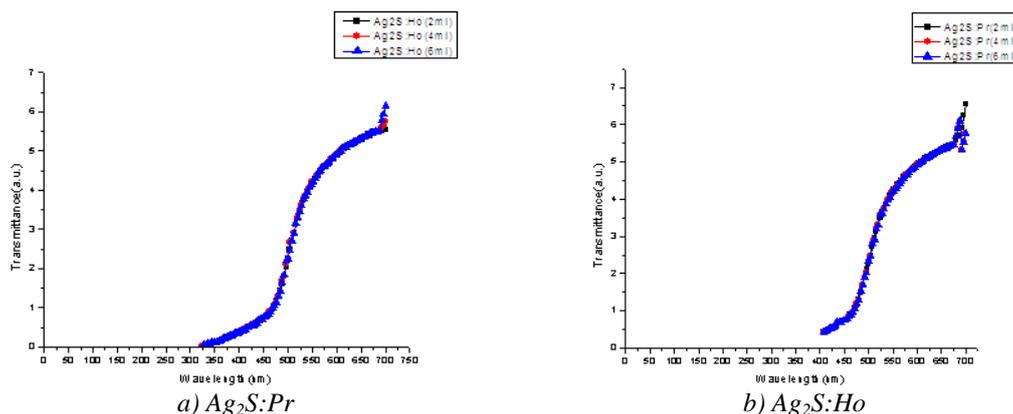


Fig. 9 Reflectance Curve of Ag_2S with different concentration of Ho, Pr

4. Conclusions

The Ag_2S : Pr and Ag_2S : Ho films prepared by chemical bath deposition (CBD) technique show good Photoconductivity properties. In the present work reported films have been successfully prepared by chemical bath deposition technique using Silver nitrate, ammonia-thiourea system. The SEM Image shows the granular and flower type structure of prepared thin film. PL spectra show that the emission occurs in visible region. We have observed that the dark current study show linear behavior and plot a curve between resistance and the voltage which is also found in linear manner in doped and undoped film.

The rise and decay 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 we conclude that the deposited Ag_2S : Pr and Ag_2S : Ho in different concentration thin films prepared by CBD technique are found to be good photosensitive and photovoltaic material. The prepared material has high transmittance in visible region. The reflectances are very low in all samples.

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