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Studies on semiconducting properties of chemically deposited doped and undoped silver sulphide film

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Abstract

Silver sulphide films were prepared by chemical bath deposition (CBD) Method in room temperature. The semiconducting Silver Sulphide thin films were deposited on the glass slide in bath containing aqueous solution of silver nitrate, thiourea, EDTA, ammonia and Pr Rare Earth. Silver nitrate used for silver ion, thiourea for sulphur ion, EDTA is the complexing agent and ammonia used for maintaining the pH. SEM micrograph indicate the presence of Flower type structure along with presence of micro particle. Photoluminescence study show the emission and absorption peak of doped and undoped film. Photocurrent, Dark current, excitation behavior and photoconductivity rise and decay studies has been done. In the Excitation spectra photocurrent exist in the ultra violet region. Quite good photosensitivity is observed in silver sulfide thin films.

Keywords: Chemical bath deposition, photoconductivity, thin films and EDTA.

Introduction

I-VI semiconductors are important nonmaterials particles with dimensions in the nanometer range used for the optoelectronic applications. Whenever the size of nano crystalline are found close to or smaller than the excition Bohr radius within the corresponding bulk material, they exhibit very special physical and chemical properties[1]. Ag_2S is an n-type material and belongs to I–VI compound. The band gap is found 1.6–3.7eV at room temperature. It is a promising material for recent era of science and technology and is very useful for the future applications such as window layers of solar cells and coatings which are sensitive to UV light.

The Chemical bath deposition method has been used for preparation of Ag_2S thin films by many researchers[2-5]. Ag_2S is a photosensitivity material. Silver sulphide show quite good photoconductivity behavior. The Photoconductivity studies of I-VI compounds are very important because of their wide applications in photonics, electronics, material science, photovoltaic solar energy conversion, thin film transistor electronics and many fields of science and technology. CBD technique has been found to be quite useful because it is low cost technique. There are very high technological values of the high photo response material only when the responses are stable and static over longer duration.

In recent era of modern science there are much attention has been shown by the researcher in the thin film like CdS, PbS, and Ag_2S due to its applications in optical and electronic systems such as photovoltaic cells, solar selective coatings, photo conducting cells, IR detectors, and high resolution optical memories. Chemical bath deposition (CBD) is the well known process and the other properties is that a prevalent low-temperature aqueous technique for depositing large-area thin films of semiconductors. It has been recognized as the simplest and most economical one. It is a technique in which thin films are deposited on different substrates immersed in dilute solutions containing metal ions and the chalcogenide source. In CBD process controlled chemical reaction to achieve for thin film deposition.

The technology used for the precipitation of the films is based on the slow controlled deposition of the desired compound from its ions in the reaction bath solution. The value of complexing agent is important in thin film science. It is acting as a catalyst and it is generally and usually employed to control the reaction in a desire medium as indicated by the pH value to obtain well define crystal structure.

Materials and methods

In the present study CBD method has been used to prepare the Ag_2S (undoped) and Ag_2S:Pr (doped) films. This method is based on slow release of silver and sulphur ions in aqueous basic solution of pH more than 10, Due to subsequent condensation of these ion Ag_2S are deposited on suitable mounted substrate. The deposition of undoped Ag_2S films was done in a chemical bath prepared in a 50 ml beaker by addition of solutions of 7 ml of 0.1 M Silver Nitrate as a source of Silver, 25ml ammonia for pH alkaline medium, 7 ml of 0.1 M thiourea as source of sulphur and EDTA used as a complexing agent.

Solutions of 0.1M thiourea and 0.1M Silver Nitrate were prepared from analytical grade chemicals. For the preparation of doped silver sulphide 2ml Pr solution of 0.01M added to the aqueous basic bath of undoped Silver Sulphide solution. Film was formed by precipitation followed by condensation on glass substrates. The thin films were prepared at a room temperature for 3 hour. The photoconductivity excitation source was an home used bulb of 60W. For the Dark current and rise and decay studies co-planar electrodes of colloidal silver are used and it were painted and dried on the surface of the films. The photocurrents were observed using a nano ammeter at an applied voltage. The films were preserved in desiccators and the Photoconductivity studies were made at different time interval. The resultant films were homogeneous, well adhered to the substrate.

Results and discussion

Sem Study: The SEM Image (Figure-2) of undoped Ag_2S film on glass substrate shows uniform distribution of particle along with some granular structure. In high magnification of undoped film the small ball like structure shows. Group of small spherically ball structure of 1micro meter size in higher magnification of micrograph shows the semicystalline size of the silver sulphide Films. The SEM micrographs of nanocrystalline Ag_2S: Pr film show more uniform distribution of particles with reduction in voids. The presence of Pr in film are more effective as a result the Image change from Ball structure to the flower type shape. The micrograph at higher magnification is very clearly shows the groups of small flowers type structure and conforms that the nano size structure.

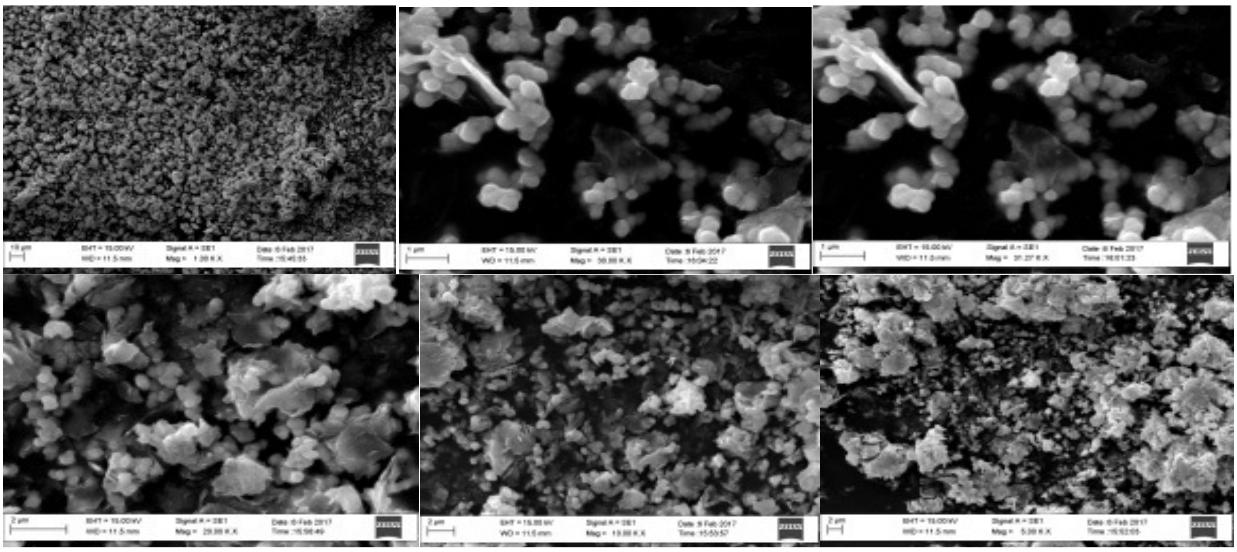

Figure-1: SEM image of Ag_2S: Pr with different magnification**.**

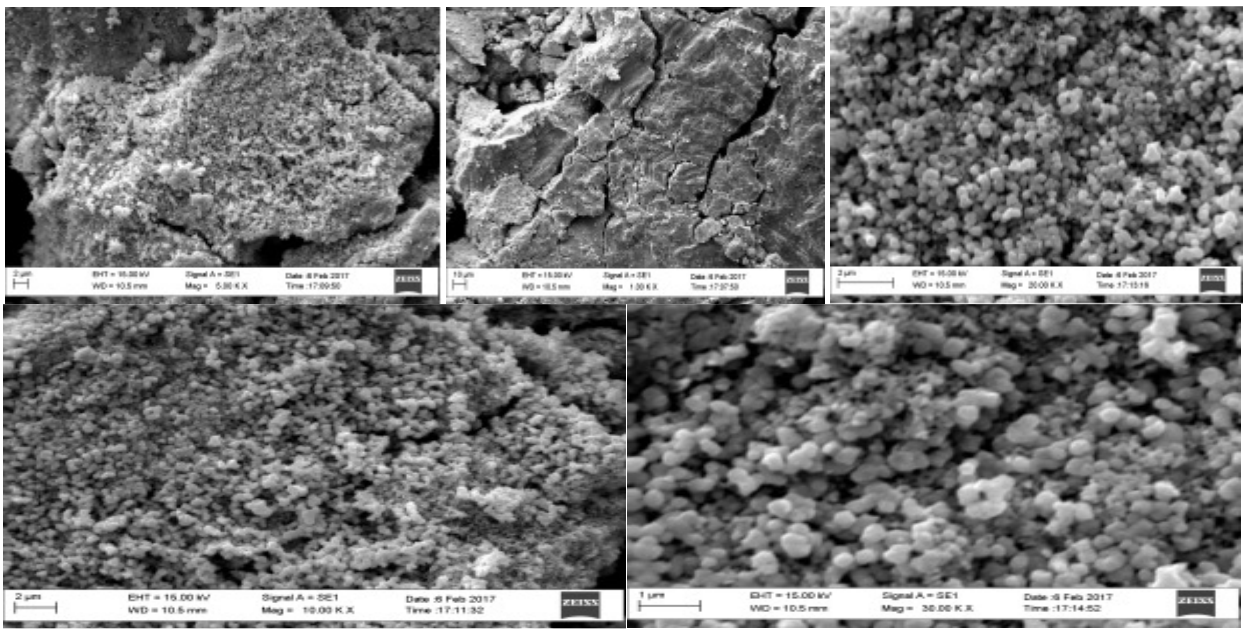

Figure-2: SEM image of Ag_2S (undoped).

Photoluminescence Study: The Photoluminescence emission and Excitation (PL) spectra of undoped and doped Ag_2S film presented in Figures 3,4,5,6. The emission were recorded under 220nm excitation wavelength. The spectra of undoped film centered at 600.22nm and 310.53nm. The PL curve are clearly shows that there is a shift in emission peak to the shorter wavelength side and also observed that the 600.22 nm wavelength found to the band to band transition which is due to the blue shift of emission of bulk Ag_2S. The PL emission spectra of semiconducting Ag_2S:Pr film shows two peaks one at 330.23nm and the other 598.98nm. According to the energy level scheme of Pr^{3+} the different emission of this ions are 295nm, 335nm, In the present study the observed peaks are not exactly same as expected for the transition in this ion. This shows that the energy transfer takes place from band of Pr to the host emitting centers. The Pr doped silver sulphide are suitable material to absorb Ultra violet(UV) radiation and convert it into the visible (598.98nm) region.

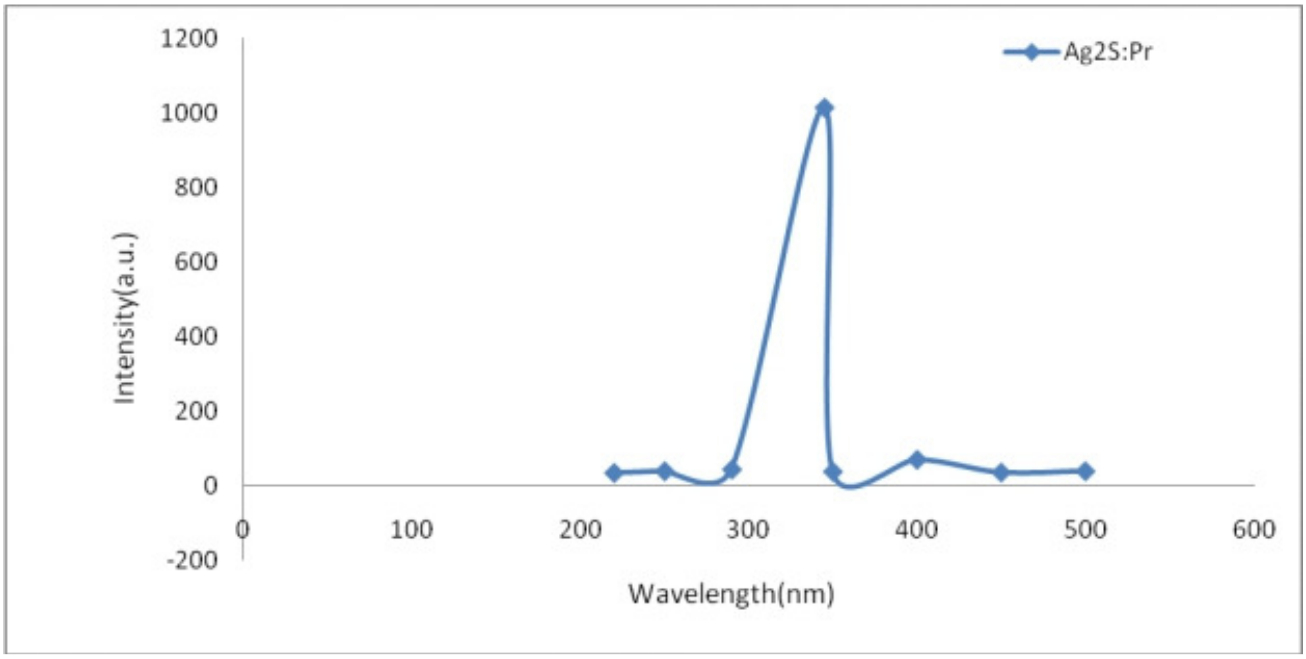

Figure-3: PL Excitation Spectra of Ag_2S:Pr.

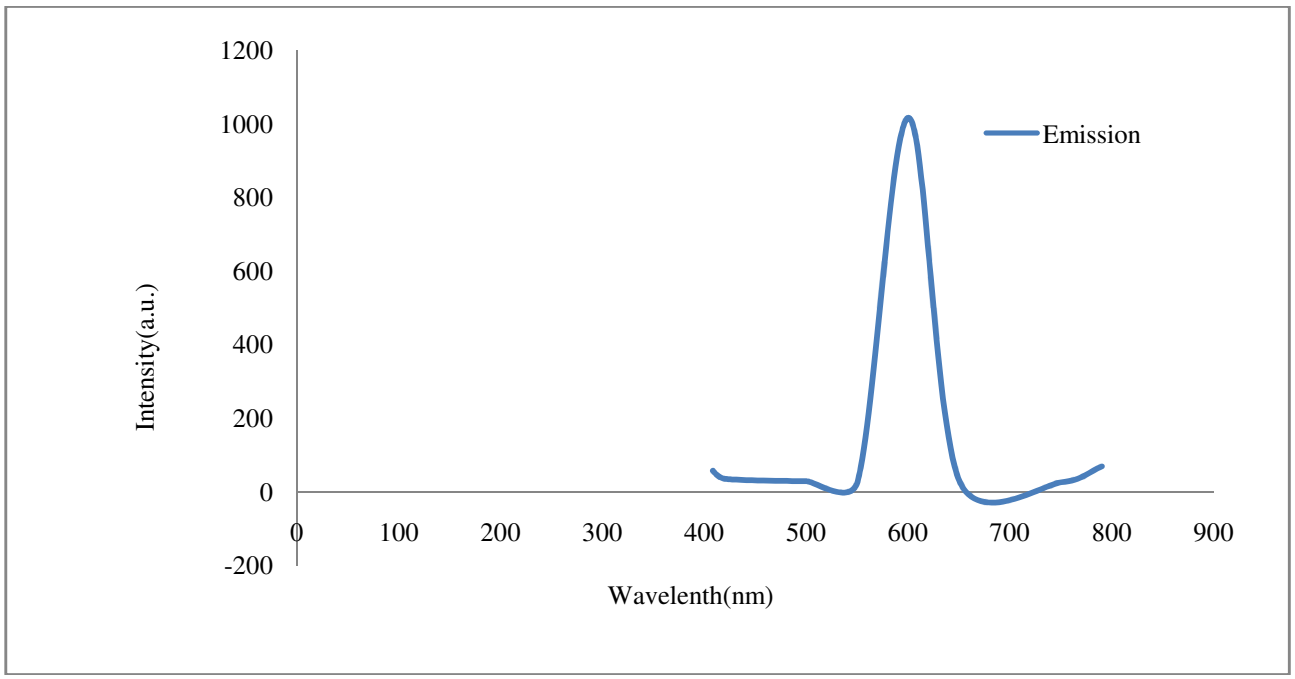

Figure-4: PL Emission Spectra of Ag_2S:Pr.

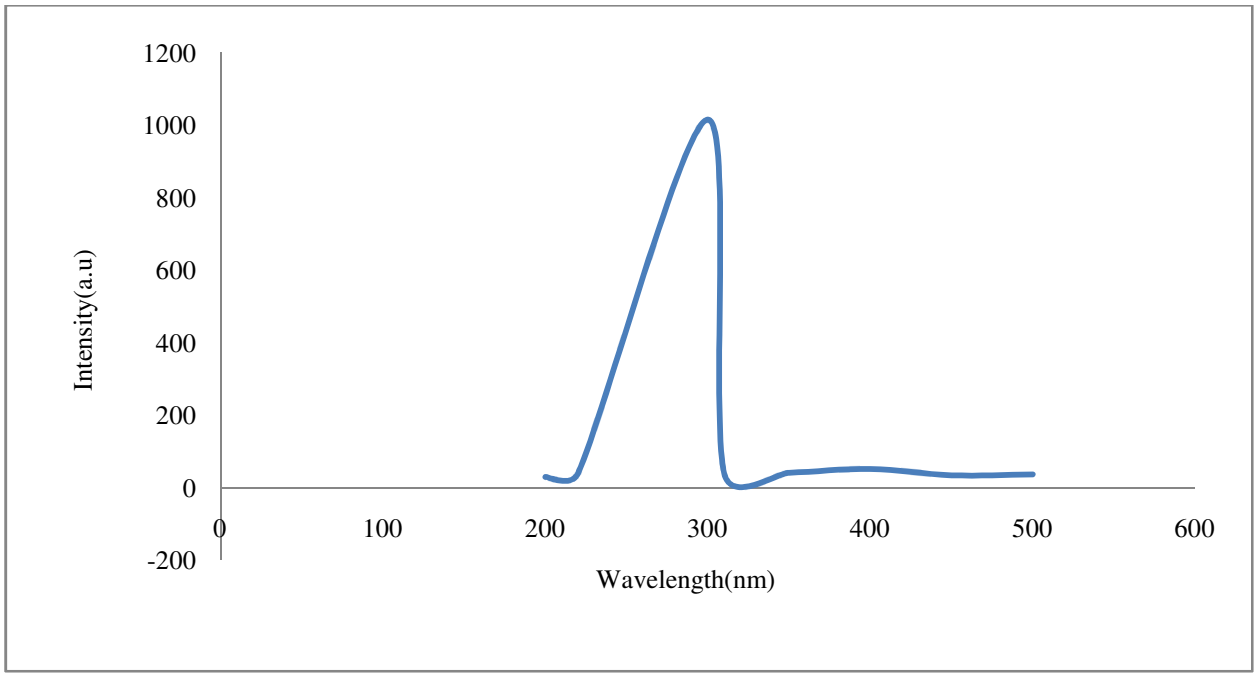

Figure-5: PL Excitation Spectra of Ag_2S.

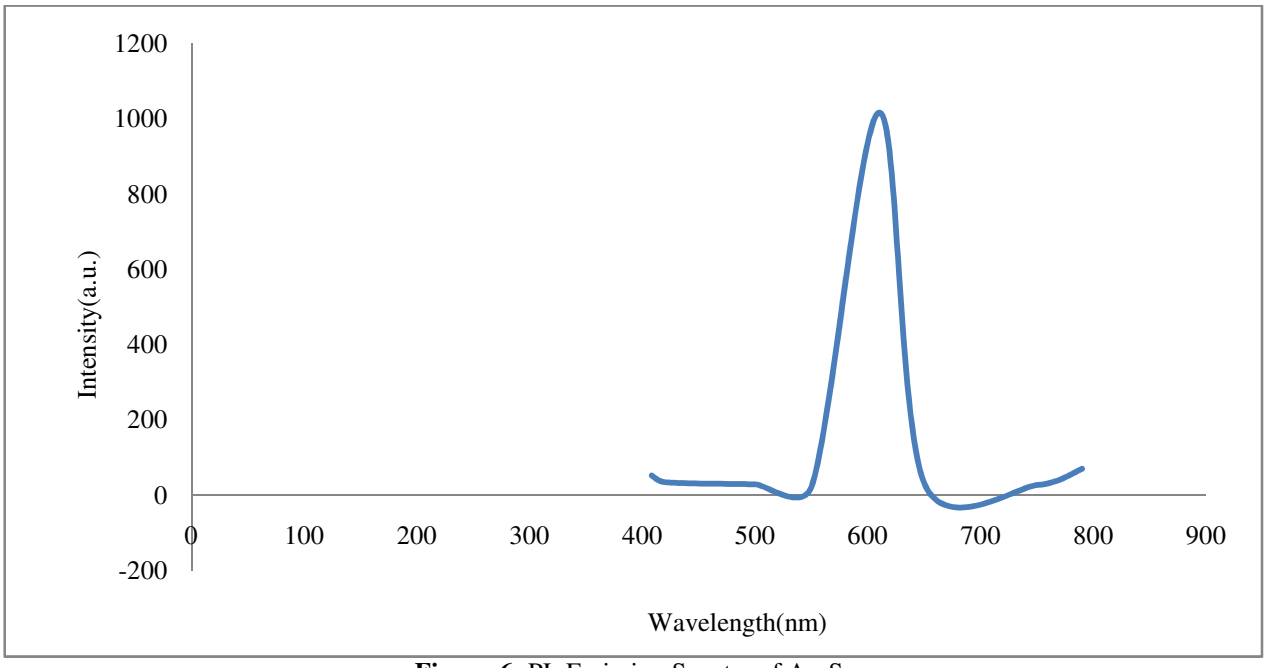

Figure-6: PL Emission Spectra of Ag_2S.

Photoconductivity Study: Dark Current study: In the present study we have observed that current will be increases with voltage in linear manner. So the dark current and applied voltage follows the ohms law. In this condition we had been form a electrode on the prepared materials and voltmeter and ammeter are connected in series. The whole place 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 dark current concept in the semiconducting thin films is the movement of thermally excited charge carriers. Some of the charge carrier are comes into the conduction band which is responsible for the conductivity. These dark current exits for limited voltage. We have observed the following relation between dark current and applied voltage.

Dark Current (I_{dc}) ∝ Applied Voltage (V_a)

$V_a = RI_{dc}$ where R is the Resistance.

Figure-7 represents the behavior of the dark current with applied voltage for Ag_2S thin films photoconductor. In all the cases a linear behavior is observed.

In Figure-8 we have calculated resistance of the samples by using formula R=V/I and plot a curve between voltage and resistance. We have found that curve is almost linear in all cases.

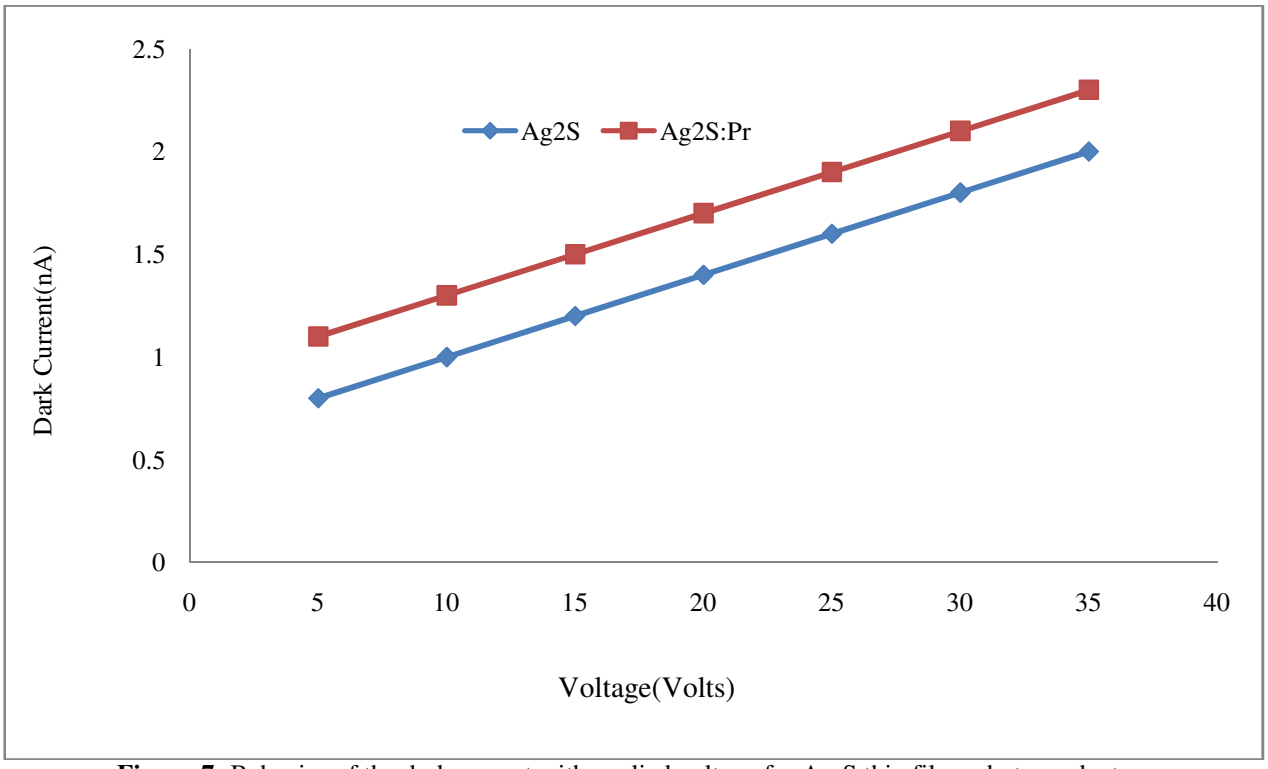

Figure-7: Behavior of the dark current with applied voltage for Ag_2S thin films photoconductor.

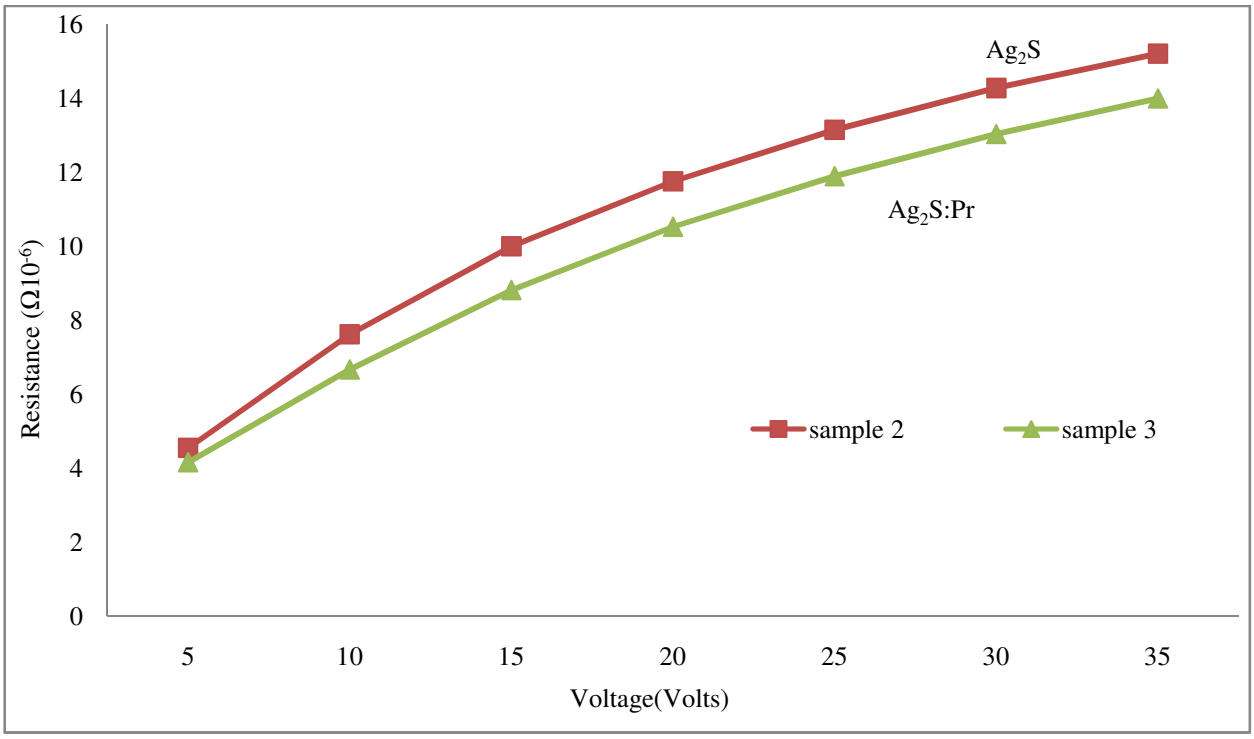

Figure-8: Plot of Resistance Vs Voltage.

Photocurrent study: The following diagram shows the rise and decay curves for Ag_2S Films prepared by CBD technique in a room temperature. All the films reported here are prepared at room temperature. The deposition time for the films was 3 hour. The rise and decay curve have been found to be similar in both sample. When radiation fall on the semiconducting thin films material the electron hole pair (photo carriers) is generated and those are responsible for the photocurrent. In the photocurrent curve, it is characterized by fast rise in the beginning followed by saturation. The initial increase in the photocurrent is due to generation of photo carries. The slowly increasing part is when recombination becomes dominant. Decay rates appeared to be slower in both undoped and doped reported Ag_2S films. The decay part of the curve follows the exponential equation. In the present study we have observed that the photocurrent increases up to 25minute (for both sample) after that photocurrent decreases. This show that silver sulphide thin films have good photo sensitive material. The current gain (photocurrent/dark current) is found to be the order of 10^4 which is quite good. It is generally believed that the photoconductivity in both undoped and doped Ag_2S thin film is of n-type due to trapping of photogenerated holes at boundaries of the negatively charged gains in poly crysattine thin films. The inter gains barrier height is lowered in this process, which enhances the electron mobility. Decay rates appeared to be slower in these films. The decay of photoexcited electron prolonged by thermal excitation from trap to the conduction band may be taken responsibility for the slow decay of the photocurrent.

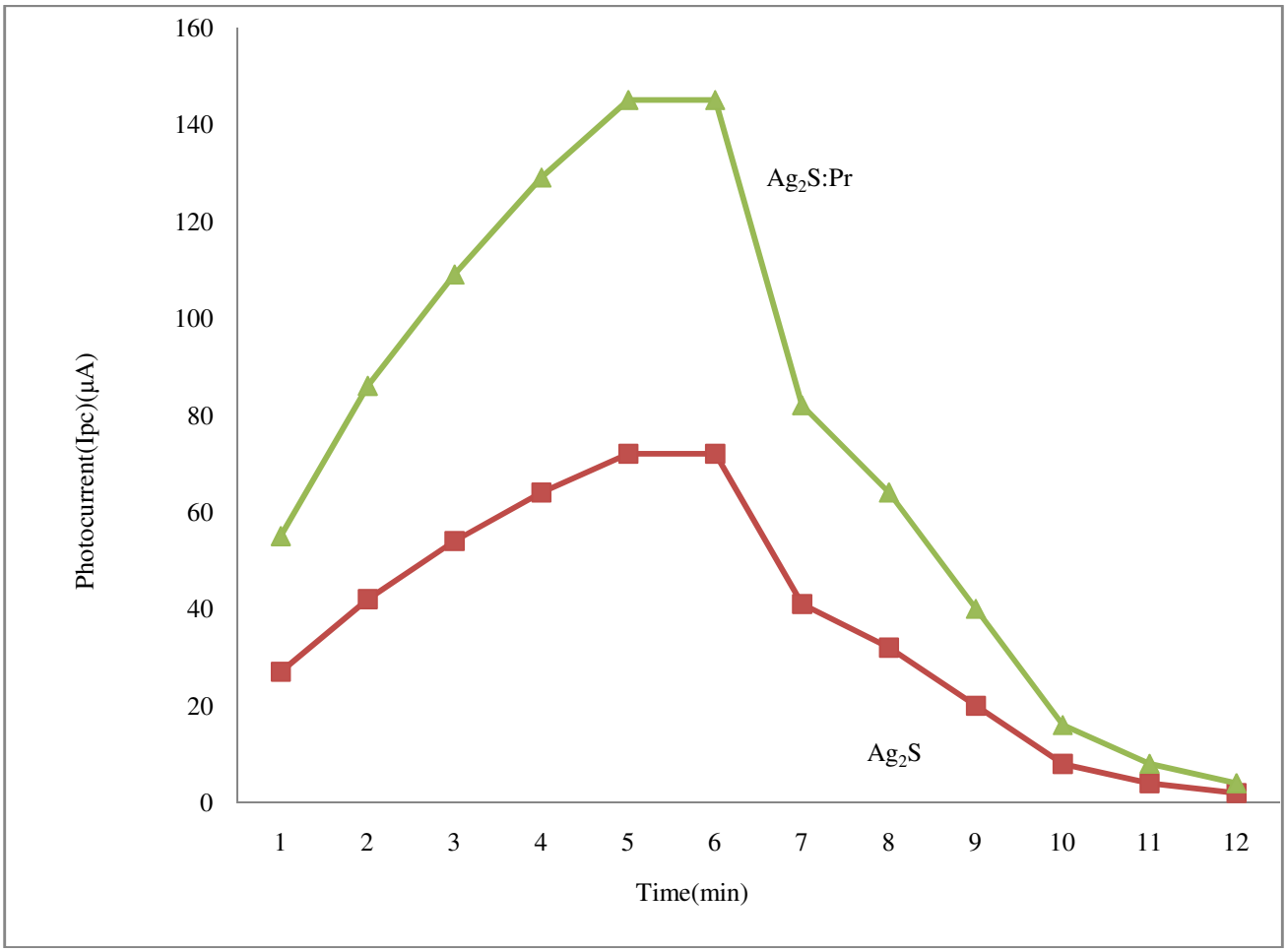

Figure-9: Rise and Decay Curve of Doped and Undoped Silver sulphide.

Table-1: Dark and photo current value of both samples.

S.N	Sample	Dark Current (I_{DC}) in nA	Photo Current (I_{PC}) in μA	Gain
1.	Ag_2S	2.1	70	0.33×10^5
2.	Ag_2S:Pr	4.2	150	0.35×10^5

Spectral studies give quite useful information. The general shapes of the samples are same. The peaks are shifted to the higher value of wavelength that indicate the band gap reduce to lower side. The excitation spectra in which plot of photocurrent is considered against wavelength or frequency of the exciting light, gives information about the nature of light near the absorption edge or different from the absorption edge. Figure-4 shows the excitation spectra of undoped and doped Ag_2S films.

Absorbance Study: In the present study we have draw the curve between absorbance (in arbitrary unit) with wavelength. The Absorbance curve (Absorbance against wavelength) of nanocystalline silver sulphide (Ag_2S) undoped and doped films prepared by CBD on glass substrate at optimize parameter all the sample gives almost the same absorbance and it is found to be in the UV region, almost each sample falls at 350nm wavelength. The silver sulphide this shows that the silver sulphide materials are important to use in photovoltaic technology.

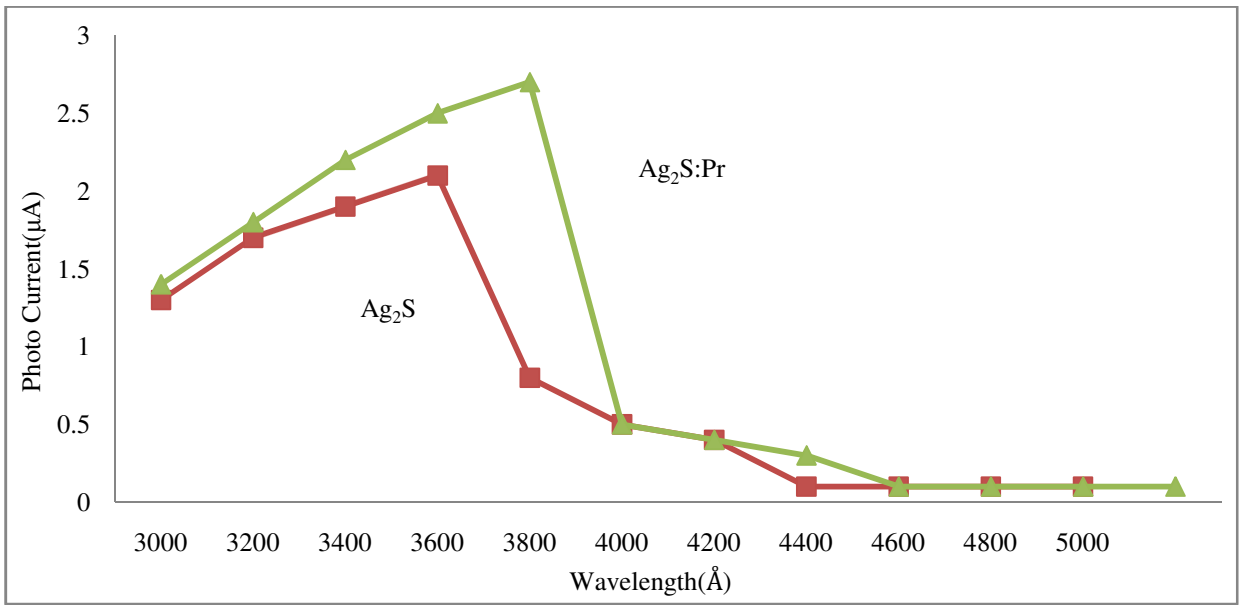

Figure-10: Excitation Spectra of Doped and Undoped Silver sulphide Film.

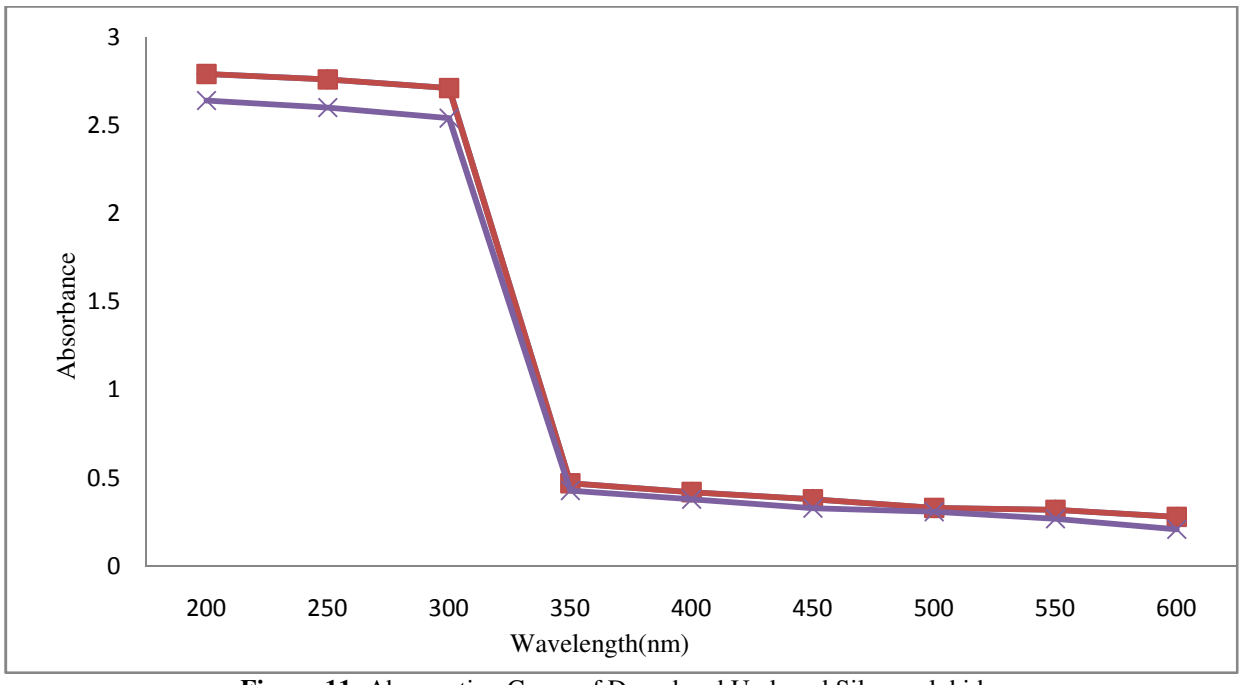

Figure-11: Aborsoption Curve of Doped and Undoped Silver sulphide.

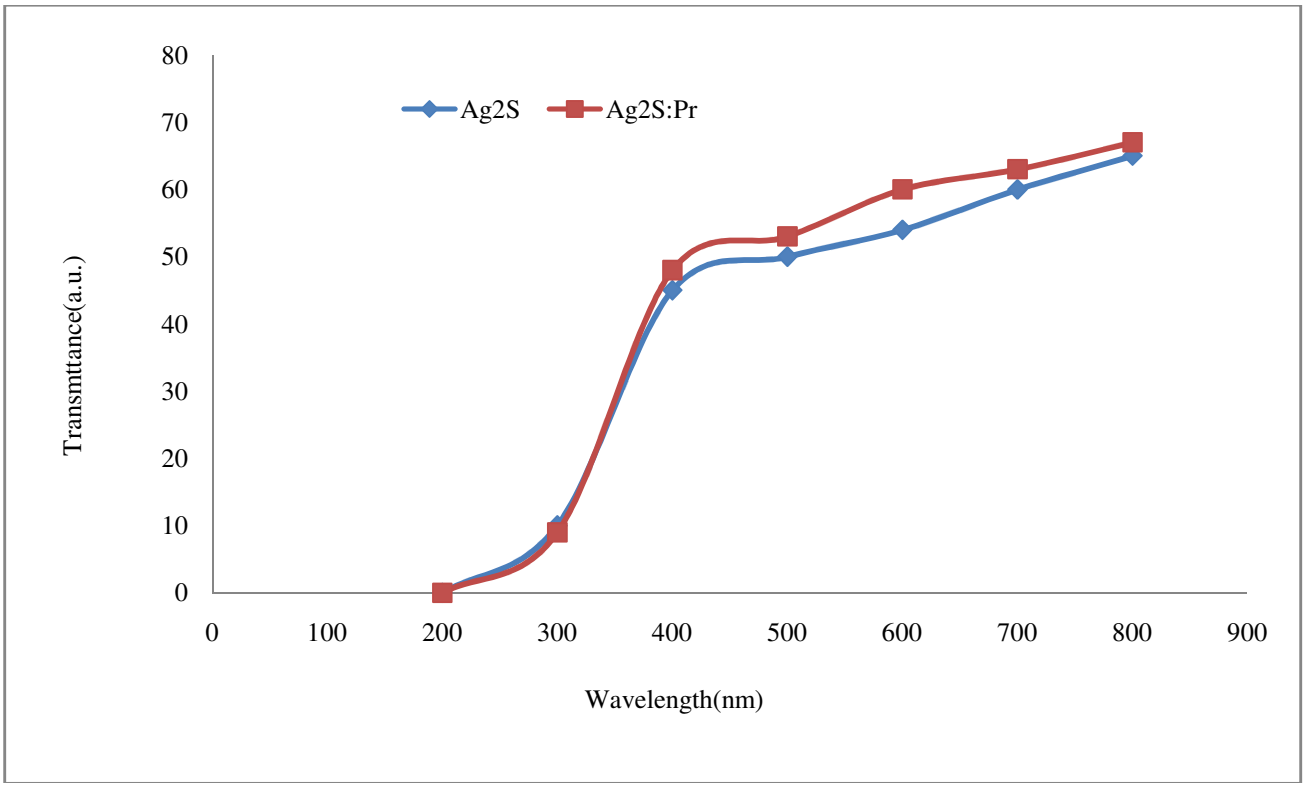

Figure-12: Transmitance Curve of Doped and Undoped Silver sulphide.

Transmittance study: The above curve shows the properties of transmittance of the silver sulphide thin films prepared by chemical bath deposition technique. It is found that the silver sulphide thin films have low transmittance in the UV regions. This type 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.

Conclusion

The doped and undoped Ag_2S films prepared by chemical bath deposition (CBD) technique show good Photoconductivity properties. In the present work Ag_2S 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 undoped and doped Silver sulphide film. PL spectra shows 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 doped and undoped Ag_2S 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 and band gap is about 3eV. So we conclude that the deposited Ag_2S thin films prepared by CBD technique are found to be good photosensitive and photovoltaic material.

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