North Maharashtra University

Proforma for Submission of Information of Final Report of the Work Done on the project

(To be submitted within two months after completion of project period)

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3. University approval no. and date: **NMU/ 11A/VCRMS/Budget-2012-13/Science-01/108/2013 Dated: 30.03.2013**

4. Tenure of the Project : **16/05/2013 to 15/05/2015**

5. Title of the project : **"Growth, Electrical & Optical Properties of n-CdSe/p- Cu_2S heterojunction thin film deposited by chemical route for photovoltaic applications".**

6. Total grant allocated : **Rs. 70,000/-**

7. Total grant received : **Rs. 55,000/-**

8. Final expenditure : **Rs. 74,885/-**

9. Objectives of the project:

To study the growth, structural, optical and electrical properties of n-CdSe /p- Cu_2S thin films by chemical bath deposition technique, and study of photovoltaic characteristics. To make the CdSe and Cu_2S thin films useful in optoelectronic applications. The development of simple, reproducible, energy intensive thin films using low cost deposition technique is an important goal of our work.

10. Whether objectives were achieved:-

The CdSe thin films was deposited by using chemical bath deposition technique successfully on glass substrate at temperature 80 ± 5^{o} C and Cu_2S thin film using chemical bath deposition technique at room temperature. The XRD pattern reveals polycrystalline nature of as-grown CdSe thin film. The crystallographic phases of sample are in good agreement with typical hexagonal wurzite structure. At room temperature, copper sulphide forms five stable phases : covellite(CuS), anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurleite($Cu_{1.95}S$) and chalcocite (Cu_2S). The SEM micrograph of all the films shows uniform morphology over entire glass substrate surface. The optical energy band gap of CdSe thin film was 1.79 eV and of a Cu_2S thin film was 2.48 eV which covers the whole spectrum of visible range is matched with reported values, electrical properties of the film shows that films were sensitive to light. The n-CdSe/p-Cu_2S junction exhibits photoconductive effect when excited by light source. The photoconductivity varies with the intensity of light it is concluded that the enhancement in photoconductivity is due to electron–hole pairs excited by the incident light. Hence these films may find use for the photovoltaic applications.

11. Summary of the findings

Introduction

In recent years much attention has been paid in developing II-VI and I-VI group materials for various optoelectronics devices such as photoelectrochemical cell, gas sensor, photoconductor, thin film transistor, γ-ray detector, large screen liquid crystal display, photodetector, etc. Cadmium selenide (CdSe) and Copper suphide (Cu_2S) are promising materials from this group. The direct intrinsic energy band gap of CdSe is ~1.7 eV and of Cu_2S is ~ 2.5 eV nearly matching with natural solar spectrum and high absorbance coefficient makes it to be used as photosensitive material.

CdSe and Cu_2S thin films can be prepared by using different methods such as chemical bath deposition (CBD), electrodeposition, molecular beam epitaxy, spray pyrolysis, successive ionic layer adsorption and reaction SILAR, MOVCD method, thermal evaporation, etc. Among these methods CBD is found as one of the best suitable technique for the CdSe and Cu_2S deposition. This method has various advantages like: 1) homogeneous films, 2) large area deposition, 3) cost effective, 4) does not require any sophisticated instruments and 5) the synthesis parameter can be easily controlled to obtain good film.

In this work, we have prepared CdSe thin films on to glass substrate by chemical bath deposition (CBD) technique at 80^0C temperature, Cu_2S thin film at room temperature and Cu_2S layer on CdSe at room temperature. Preparative parameters such as concentration of cationic and anionic precursor solutions, pH of the solution, temperature of reaction bath, complexing agent and deposition time are optimized to get good quality adherent and uniform thin films. The as-deposited CdSe, Cu_2S and Cu_2S layer on CdSe thin films were characterized for their structural, surface morphological, optical, electrical properties, and photosensitivity of the films.

Experimental Details

CdSe and Cu_2S thin film were deposited on glass slides of dimension 7.3 cm x 2.5 cm x 0.2 cm provided by Blue Star Ltd, Mumbai, India were used as the substrates. Chemicals used for preparing CdSe thin films were as follows:

Deposition of CdSe thin films

A. R. grade cadmium sulphate $[CdSO_4].H_2O$ was used as a cationic precursor solution. For maintaining the pH of the precursor solution ~ 10, NH_4OH solution was used. Sodium sulphite (Na_2SO_3) and selenium powder was used as a solving agent for anionic precursor solution supplied by Loba Chemie, Mumbai. All solutions were prepared in deionized water.

A solution of sodium selenosulphite (Na_2SeSO_3) was prepared by refluxing 100 ml of 0.1 M sodium sulphite with selenium powder for about 5-6 h. It was sealed and kept overnight, since on cooling, small quantity of selenium settles down at the bottom of the solution. It was then filtered to obtain a clear solution.

Cadmium selenide thin films were deposited on a glass substrate at a bath temperature 80 ± 5^0C for 3h. 0.1M of cadmium sulphate $[CdSO_4].H_2O$ and sodium selenosulphite (Na_2SeSO_3) are taken in equal proportion in glass beaker. The pH of the resultant mixture was kept 10 by addition of ammonia with the constant rate (2 ml/min) and constant stirring. The cleaned glass substrates were dipped vertically in the beaker. The films that were grown found to be uniform, well adherent to the substrate and red-orange in color.

Deposition of Cu_2S thin film

A. R. grade cupric sulphate ($CuSO_4$) was used as a cationic precursor solution, For maintaining the pH of the precursor solution ~ 10, NH_4 OH solution was used. Thiourea $(CS)[NH_2]_2$ was used as anionic precursor solution supplied by Loba Chemie, Mumbai. All solutions were prepared in deionized water.

Volumetric calculations of reactants were made for Cu_2S deposition; 20 ml of 0.05M cupric sulphate and 0.05M thiourea were taken. The pH of the resultant mixture was kept ~ 10.2 by the addition of ammonia with the constant rate (2 ml/min). The temperature of the reaction bath was maintained at room temperature for 70 minutes. This layer of Cu_2S was deposited on CdSe thin films at room temperature.

5.2.5 Characterization of CdSe and Cu_2S films

Thin films of CdSe and Cu_2S were characterized for structural, compositional, surface morphological and optical properties. The film thickness measurement of CdSe and Cu_2S thin films were carried out by interferometer technique. The structural analysis of the films were made by an X-ray diffractometer (Bruker AXS, D8 Advance, Germany, Cu-K_α radiation at λ = 1.5406 Å) in the 2θ range 20–80^O. The surface morphology and composition was studied by scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX) using JEOL-JSM 5600, respectively. A double beam spectrophotometer (Perkin Elmer UV–Vis spectrophotometer Lambda 25 with automatic computer data acquisition) was employed to record optical spectra over the wavelength range of 300–1100 nm, at normal light incident. Photosensitivity property of CdSe and Cu_2S films were studied by I-V curves (Keithaly Ltd. interfaced with computer) in dark and under illumination with in visible range.

Result and Discussions

CdSe Thin Film

X-ray diffraction (XRD)

The CdSe thin films may grow with either sphalerite cubic (zinc-blende type) or the hexagonal (wurtzite-type) structure. The hexagonal state is the stable phase of CdSe, while sphalerite cubic modification is a metastable structural phase commonly occurring at low temperature. Fig. 1 gives the XRD pattern of the as-deposited CdSe thin film. The broad hump in the background is due to amorphous glass substrate and also possibly due to some amorphous phase present in the CdSe thin film. The XRD pattern reveals polycrystalline nature of as-deposited material. The diffraction peaks at $2\theta = 25.87^0$ and 42.67^0 are attributed to (002) and (110) planes, respectively of hexagonal CdSe as can be seen in comparison with the JCPDS Card No. 08-0459. The various structural parameters for CdSe thin films are calculated using standard formulae and are systematically represented in Table No. 1. The lattice parameters calculated matches very well with the standard values reported by other workers.

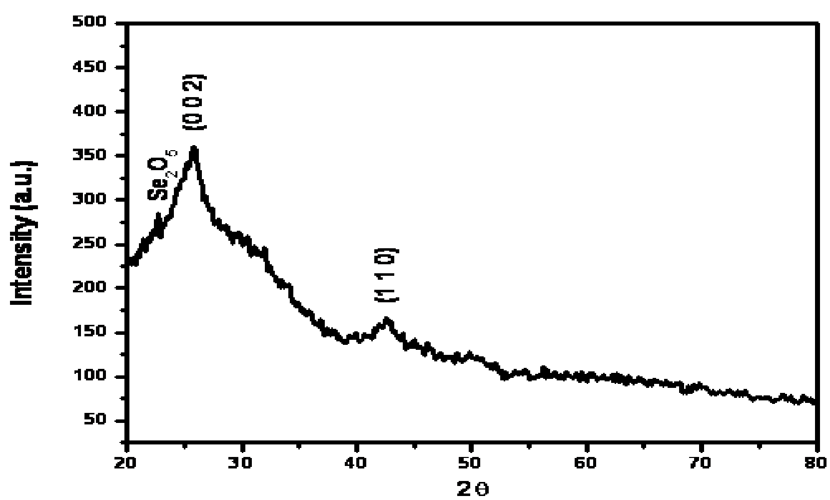

Fig. No.1 X-ray diffraction pattern of as –deposited CdSe thin film.

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Table 1 Structural parameters of CdSe thin films.

Composition	2θ (deg.)	d (Å)	(hkl)	a(Å)	c(Å)
CdSe	25.87	002	3.5100	--	7.02
	42.67	110	2.1510	4.302	--

Scanning electron microscopy (SEM)

Surface morphology of CdSe thin films were carried out using scanning electron microscopy (SEM) and it is shown in fig 2. The SEM micrograph of the film shows uniform surface morphology over the entire glass substrate surface. The presence of fine grain background is an indication of one-step growth by multiple nucleations. The image consists of dense layer with small crystallites. Some large particles of approximately 460 nm in size are embedded on the surface. Those particles are quite likely colloidal particles formed in the solution and adsorbed on the substrate during the growth of the film.

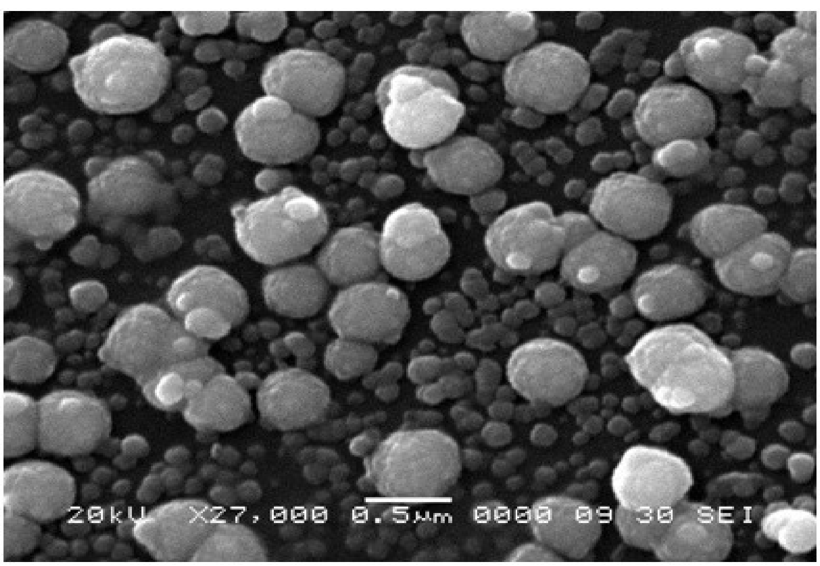
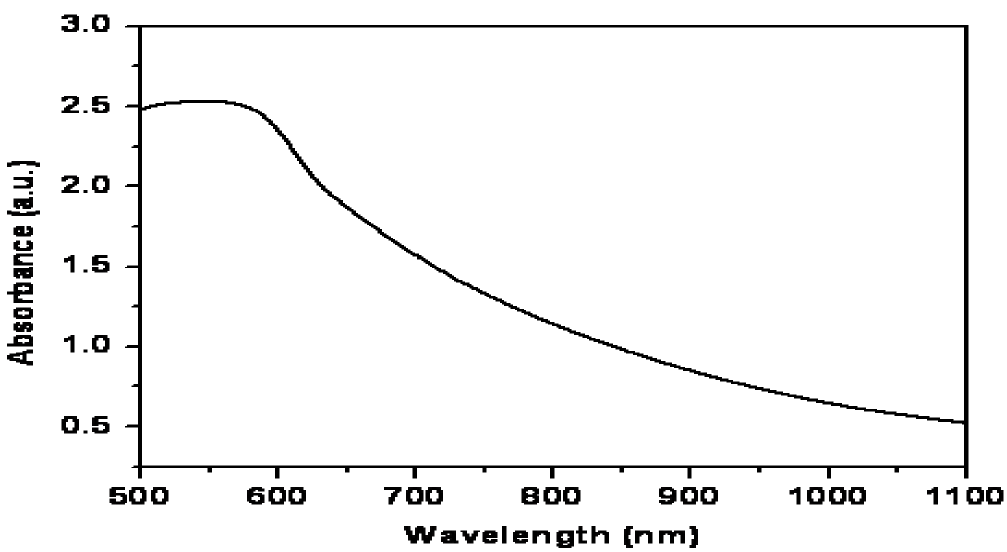


Fig. No. 2 SEM image of as-deposited CdSe thin film.

Optical analysis

Optical absorbance spectra were used to study the optical transition of as-deposited CdSe thin films deposited on glass substrate. Fig. 3 shows the variation of optical absorbance (αt) with wavelength (λ). Study of materials by means of optical absorption provides a sample method for explaining some features concerning the band structure. The optical absorbance spectra were studied at room temperature in the range of wavelength 300-1100 nm. It is clearly seen from the optical spectra that the absorption edge shifts towards a longer wavelength for the as deposited thin film. The relation between absorption coefficient 'α' and the incident photon energy 'hν' can be given as $\alpha = \frac{A(h\nu - E_g)^n}{h\nu}$ Where 'A' is constant. Eg is optical band gap of the material and the exponent 'n' depends upon the type of transition. The values of 'n' for direct allowed, indirect allowed and direct forbidden transition are n = ½, 2 and 3/2 respectively. Fig. 4



shows CdSe thin film energy band gap is 1.79 eV.

Fig. 3 Absorbance of CdSe thin film

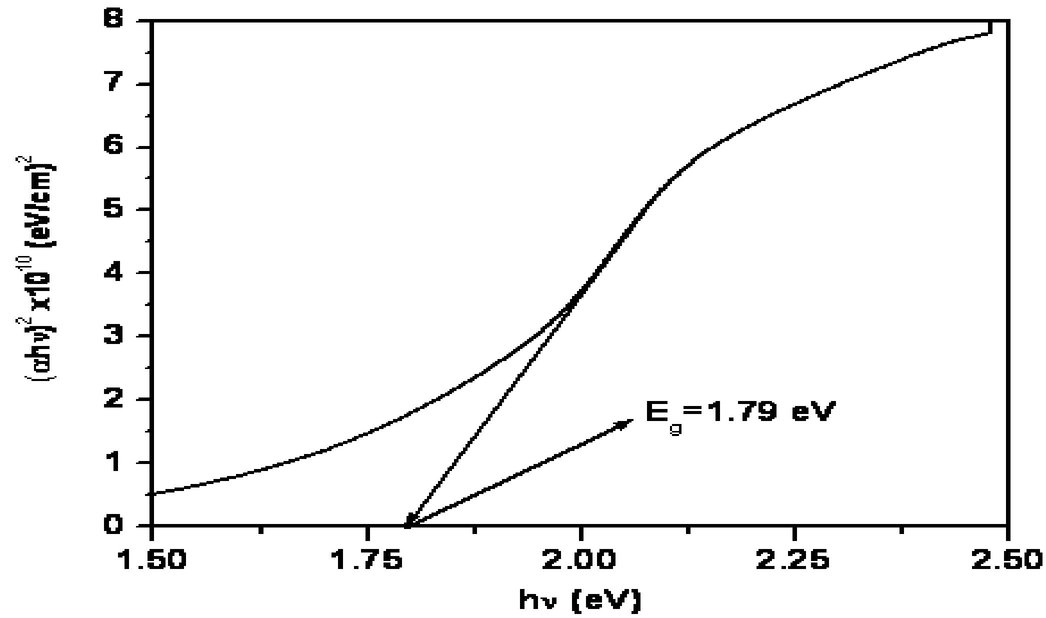


Fig. No. 4 Optical energy band gap of CdSe thin films

Fig. No. 3 Absorbance of as-deposited CdSe thin film.

I–V characteris...

To study electrical properties of binary CdSe thin films. We measured the current-voltage (I–V) characteristics at room temperature. It was observed that the current is proportional to the applied voltage suggesting the ohmic behavior. From the plot (Fig. 5) the room temperature electrical resistivity was found out to be 55.74 $\times 10^3$ Ω-cm.

Photo response

The photosensitivity property of CdSe was studied by I–V curve in dark and under illumination with different light intensities. The distance between 100 watt bulb and sensor was varied to change the intensity of light. Fig. 5 shows I–V plot of sample in dark and under illumination for intensities 7000 and 11000 Lux. The change in I-V plot with change in intensity of light suggests that the samples can be employed for photosensor applications. The resistivity of the film in dark was 55.74×10^3 Ω-cm and upon illuminating the film for 11000 lux its resistivity decreases to 44.44×10^3 Ω-cm.

For the photosensor characterization of the film, photosensitivity is an important parameter which calibrates directly the quality of the photosensor. The photosensitivity is calculated by using the equation as

$$S = \frac{I_{ph} - I_d}{I_d}$$

where I_d and I_{ph} are the dark and photo current respectively.

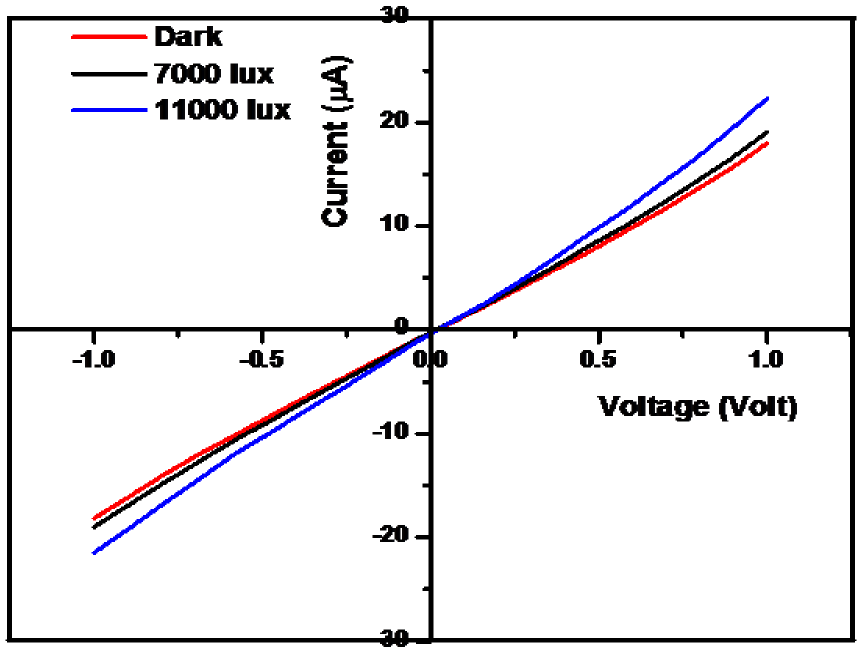


Fig. No. 5 I-V Characteristic of CdSe thin film in dark and under illumination.

Cu_2S Thin Film

Optical analysis

Optical absorbance spectra were used to study the as-deposited Cu_2S thin films deposited on glass substrate. Fig. 6 shows the variation of optical absorbance (αt) with wavelength (λ). Study of materials by means of optical absorption provides a sample method for explaining some features concerning the band structure. The optical absorbance spectra were studied at room temperature in the range of wavelength 300-1100 nm. It is clearly seen from the optical spectra that the absorption edge shifts towards a longer wavelength for the as deposited thin film. The relation between absorption coefficient 'α' and the incident photon energy 'hν' can be given as

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

Fig. 4 shows Cu_2S thin film energy band gap is 2.48 eV.

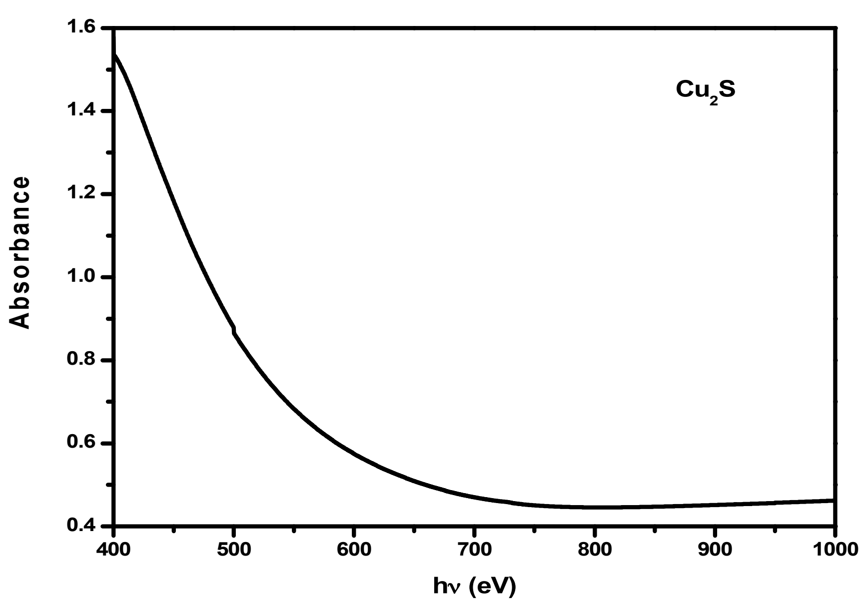


Fig. No. 6 Absorbance of as-deposited Cu_2S thin film.

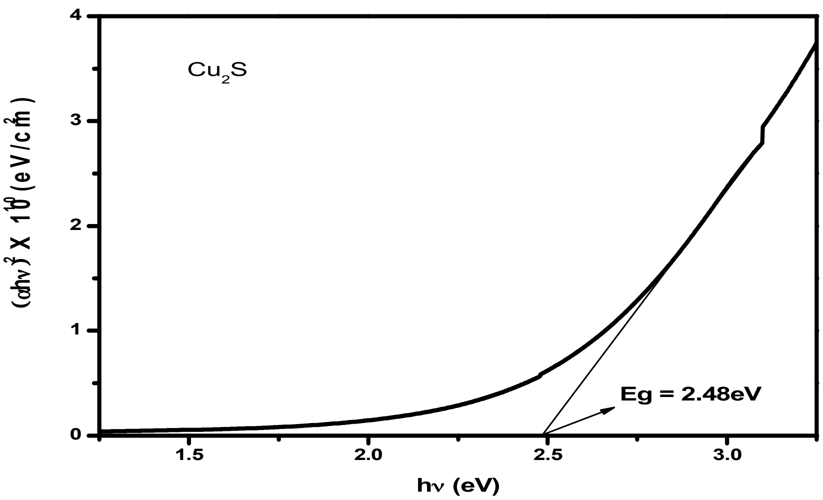


Fig. No. 7 Optical energy band gap of Cu_2S thin films

I–V characteristics

To study transport properties of binary Cu_2S thin films. We measured the current-voltage (I–V) characteristics at room temperature. It was observed that the current is proportional to the applied voltage suggesting the ohmic behavior. From the plot (Fig. 8) the room temperature electrical resistivity was found out to be 87 Ω-cm.

Photo response

The photosensitivity property of Cu_2S was studied by I–V curve in dark and under illumination with different light intensities. The distance between 100 watt bulb and sensor was varied to change the intensity of light. Fig. 8 shows I–V plot of sample in dark and under illumination for intensities 7000 and 11000 Lux. The change in I-V plot with change in intensity of light suggests that the samples can be employed for photosensor applications. The resistivity of the film in dark was 87 Ω-cm and upon illuminating the film for11000 lux its resistivity decreases to 66 Ω-cm.

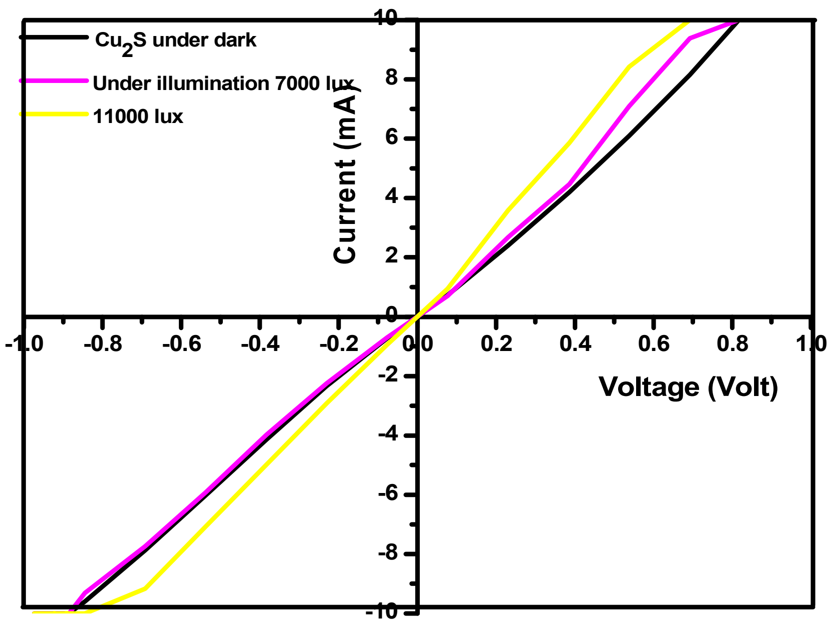


Fig. No. 8 I-V Characteristic of Cu_2S thin film in dark and under illumination.

Cu_2S layer on CdSe Thin Film

The n-CdSe/p-Cu_2S junction exhibits photoconductive effect when excited by light source. The variation of photocurrent with respect to the applied voltage for light intensity 7000 lux as shown in fig. 9.The characteristics indicate a diode like behavior of the junction, The photoconductivity varies with the intensity of light it is concluded that the enhancement in photoconductivity is due to electron –hole pairs excited by the incident light. Hence these films may find use for the photovoltaic applications.

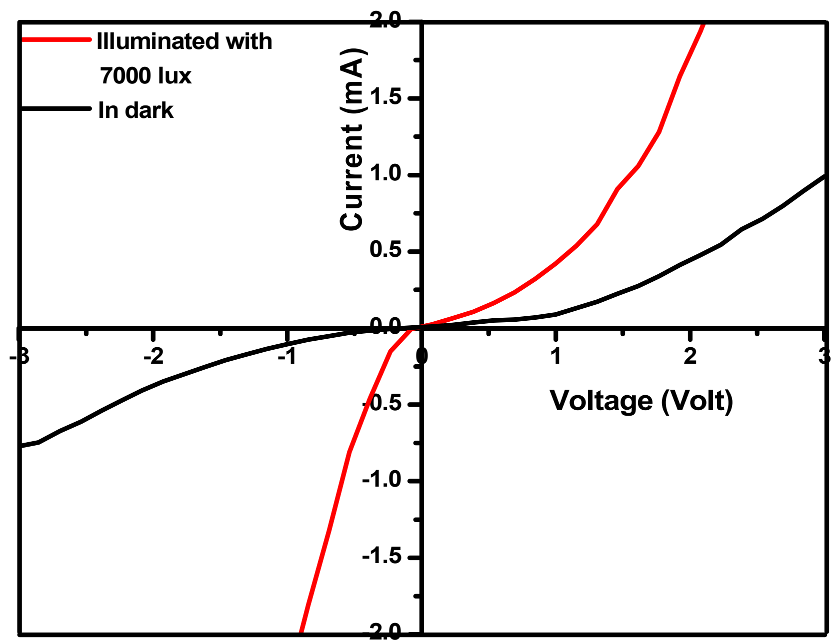


Fig. No. 9 I-V Characteristic in dark and illumination at 7000 lux light intensity for n-CdSe/p-Cu_2S thin film .

12. Future Scope : CdSe and Cu_2S are can be used as a TiO_2 sensitizer.

Principal Investigator **Principal**