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Photoconductivity studies of hybrid ZnTe/MgPc thin films prepared by physical vapour deposition

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ABSTRACT

The novel hybrid ZnTe/MgPc thin films of thickness 300 nm – 400 nm were prepared by vacuum deposition technique at 10^{-5} Torr. The as deposited films on glass substrates at the room temperature were annealed upto150ºC in order to ensure crystalline phase of the hybrid. The optical studies indicate enhancement of optical absorption of magnesium phthalocyanine by consistently increasing zinc telluride in ascending proportion. Consequently broadening of absorption range from visible to near IR region was found which resulted in increased photoconductivity for the compound. The activation energy proportionally decreased from 2.25 eV to 1.9 eV. The SEM images of the films show very smooth surface morphology devoid of pinholes and grain boundaries complimenting photoconductivity enhancement. EDAX results confirm the presence of magnesium in the hybrid thin film. The band gap is reduced from 2.6eV to 1.5eV. Annealing upto an optimum temperature results in enhancement of photoconductivity.

Keyword: photoconducity, thin film, annealing, vacuum evaporation.

INTRODUCTION:

Zinc Telluride (ZnTe) is a II-VI compound semiconductor having a direct band gap of 2.26 eV at room temperature [1, 2]. Specifically, for bright light emitting diodes (LED), ZnTe is a promising candidate since the emission wavelength corresponds to the maximum sensitivity of the human eye [3]. Polycrystalline ZnTe films were also used in tandom solar cell structures [4]. Applications to photovoltaics proved that ZnTe is promising for the production of high efficiency solar cells [5, 6].

Magnesium Phthalocyanine (MgPc) is a P-type semiconductor with a band gap of 2.6 eV [7], exhibiting high chemical and thermal stability. Metal Phthalocyanines are used in many fields of industry as semiconducting devices, solar cells, liquid crystals, photovoltaic cell, gas sensors and optical data storage [8].

Most phthalocyanine compounds are insoluble in common organic solvents and so it is difficult to prepare them by solution casting techniques. Hence, very often, thin films of phthalocyanines (MgPc) are made by vacuum sublimation technique. This method has the advantage of producing high purity films [9]. In the present work a compound photoconductor has been attempted using ZnTe and MgPc. In this paper, optical absorption, photoconductivity, thermal activation energy, optical band gap and their dependence on annealing for compound ZnTe/MgPc thin films are presented.

MATERIALS AND METHODS

ZnTe and MgPc (Aldrich) were mixed together (in the ratio of 60:10, 70:10, 80:10, 90:10, 100:10 mg respectively) and ground well for several hours, before sublimed in vacuum (Hind Hivac 12 A4-D) at a pressure of 10^{-5} Torr. Glass substrates used were first cleaned thoroughly with liquid detergent; then washed with distilled water; and agitated ultrasonically in acetone. Finally the substrates were dried in hot air. The coated films were air annealed at 150°C to attain crystallinity. Thickness measurements were recorded using Surface Profilometer (Dektak 6M, M/S. Veeco, USA). UV-VIS absorption spectra of the films were recorded using UV-VIS spectrophotometer (Schimuzu UV-2450). Photoconductivity and temperature dependent conductivity were measured using Kiethley picoammeter (model 6485).

RESULTS AND DISCUSSION

For ZnTe/MgPc thin films deposited onto glass substrates, we could experimentally establish that the samples obtained stable structure and they exhibited reproducible optical and photoconductive properties provided they were subjected to annealing. These heat treatments consisted of several successive heating-cooling cycles within a temperature range, 300-500 K [10].

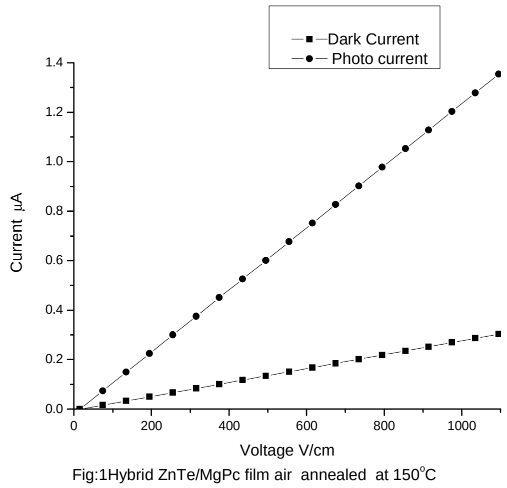


Fig:1. Field dependent Dark and photoconductivity of Hybrid ZnTe/MgPc film.

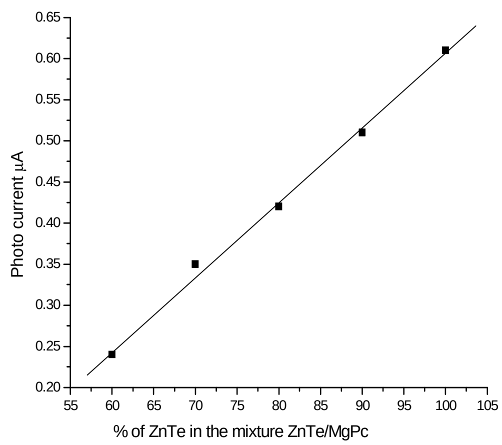


Fig:2 Percentage of ZnTe in compound ZnTe/MgPc Vs Photo current.

Fig.1 shows the field dependent dark and photocurrent plots for hybrid ZnTe/MgPc thin films. Linear increase of dark and photocurrent was observed for the samples. There was a significant rise in photocurrent over dark current, when the sample was illuminated with visible light (100 watts halogen lamp). The enhancement of photocurrent in hybrid film is due to its capability to absorb over all regions of visible light.

Fig.2 shows the increase in photocurrent with change in concentration of ZnTe. It is observed that the photoconductivity increases with increase in concentration of ZnTe.

Fig.3 shows the variation of dark current with temperature for the thin film samples. The temperature was varied in the range 30°C-150°C for constant applied field of 500V/cm. The plots indicate the exponential increase of temperature dependent current confirming the semiconducting nature of the samples. From the lnI versus 1/KT plot, the activation energies of various concentration of ZnTe (60:10, 70:10, 80:10, 90:10, 100:10) in the hybrid ZnTe/MgPc films were calculated as 2.71eV, 2.3eV, 1.802eV, 1.627eV and 1.34eV respectively.

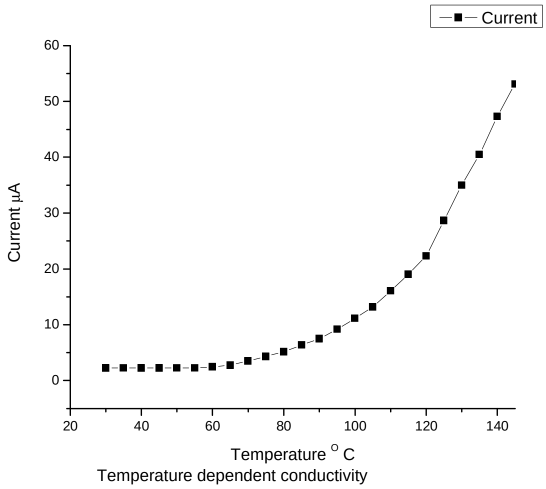


Fig:3 Variation of dark current with temperature.

The activation energy is found to decrease with increase in concentration of ZnTe in the hybrid ZnTe/MgPc combination.

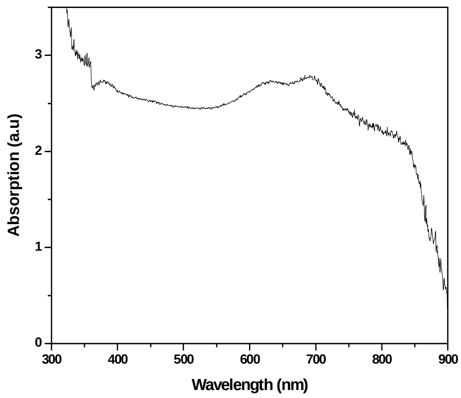


Fig:4 Absorption spectra of Hybrid ZnTe/MgPc air annealed at 150°C.

Fig:4 shows the absorption spectra of hybrid ZnTe/MgPc thin film air annealed at 150°C. It is observed that the hybrid thin film have a very wide absorption range over whole visible region with a significant peak at 700 nm. The air annealed sample has a better absorption compared with as deposited thin films.

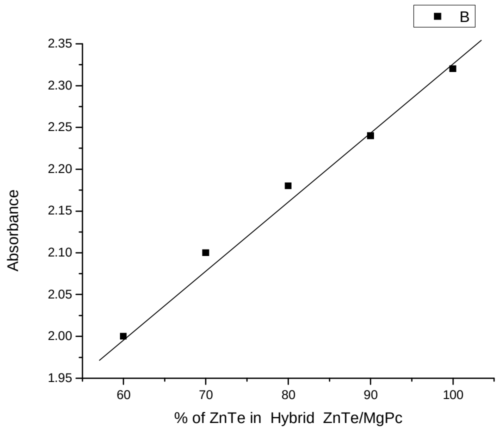
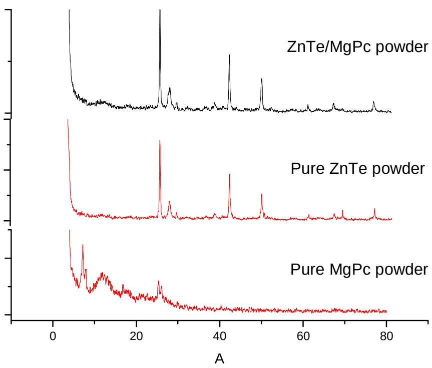


Fig:5 Variation of absorbance with conc (60, 70,80,90,and 100mg) of ZnTe in Hybrid ZnTe/MgPc.

Fig.5 shows the absorbance versus concentration of ZnTe. It is observed that as concentration of ZnTe increases, absorbance increases.

X-ray diffraction analysis:
The ZnTe powder,as well as thin film, MgPc doped film all corresponds to cubic form of ZnTe. ZnTe crystal unit cell dimension is 6.08 A^0. The Face centered cubic system has four lattice points and volume corresponds to one lattice point is 56.18 ^{A03}.



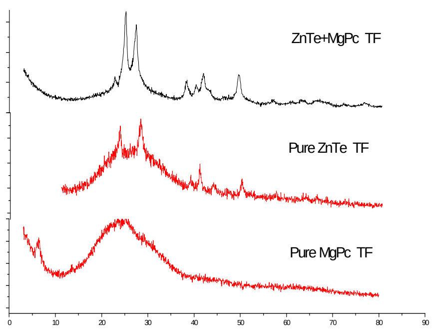


Fig:6 (a) **Fig:6 (b)**

Fig:6 (a) Powder XRD of MgPc, ZnTe and hybrid ZnTe/MgPc Powder.
Fig:6 (b) XRD of MgPc, ZnTe and hybrid ZnTe/MgPc Thin Film.

MgPc crystallizes in monoclinic system with cell parameters 14.368A^0, 4.898A^0, β = 119.86^0 with unit cell volume of 1153$A^{0\,3}$. The average volume occupied by a molecule is 288A^{03}.

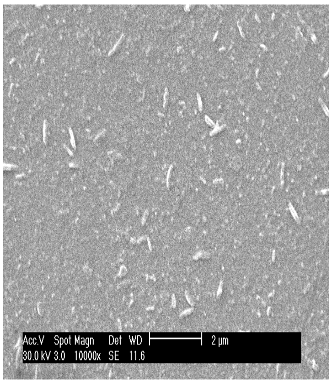
These crystal data show that the phthalocyanine molecules cannot replace ZnTe molecules in the ZnTe lattice. As MgPc volume is much higher than the primitive cell volume of ZnTe, interaction between these two substances in the thin film is possible only through surface interactions. This is evident from the SEM micrograph of doped thin films.

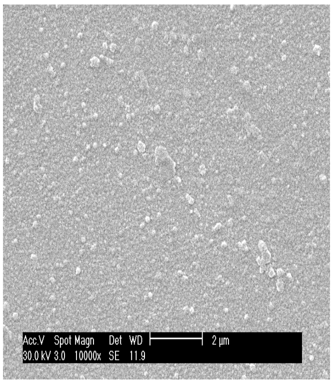
The powder diffractogram of the thin film shows the peaks corresponding to ZnTe only. It may be inferred that the MgPc molecules/particles are randomly distributed on the surface of ZnTe thin film with no individual crystal regions.

However the possibility of some Magnesium and Zinc atoms or some Magnesium atoms from Phthalocyanine exchanging positions with Zinc in the telluride cannot be ruled out.

The ZnTe lattice might be containing a small percentage of Magnesium atoms in the position of Zinc atoms. This could have changed the physical properties.

SEM Analysis:





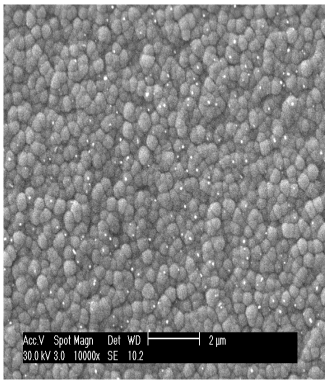


Fig: 7(a) 70:10 **Fig 7(b) 80:10** **Fig(c) 100:10**

Fig:7(a),7(b)and7(c) SEM Micrograph of ZnTe: MgPc-70:10mg, 90:10mg and 100:10mg TF

Using Scanning Electron Microscope (SEM), highly magnified pictures of the hybrid thin film samples are taken over various regions and different magnifications. Fig.7(a) and Fig.7(b) and Fig. 7(c) shows the SEM results of the samples.

By analyzing through the pictures, the film is uniformly distributed for both Pure ZnTe and MgPc thin films. Surface of the films are very smooth and there is no pinhole observed. The grain boundaries are also not observed. Which suggest that the film is a good photoconductor.

It can be seen from the picture that ZnTe and MgPc are mixed uniformly in the hybrid samples and surface of films are observed smooth.

EDAX Analysis:

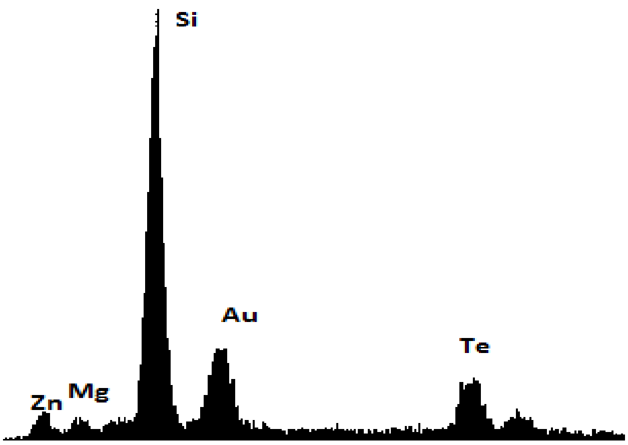


Fig:8 EDAX results for ZnTe: MgPc-100:10mg TF

EDAX results are shown in Fig:8. Elements present in the thin film are Silicon (Si), Gold (Au), Tellurium (Te), Magnesium (Mg) and Zinc (Zn). Since we use glass substrate for forming thin films Si is observed maximum and during characterization of EDAX, the sample is gold plated. These are the reason for having maximum percentage of Si and followed by gold Au. The elements of ZnTe are present and that of MgPc, magnesium is present but the elemental composures of Pc were not able to detect.

Determination of Band Gap:

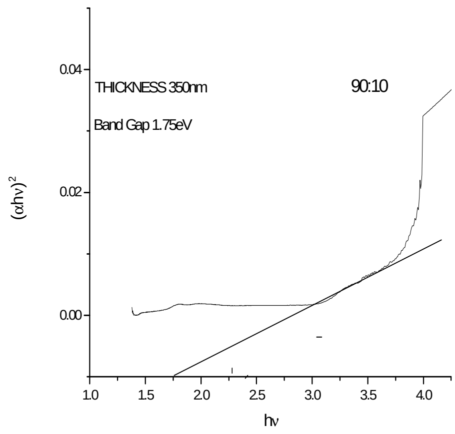


Fig:9 (a)

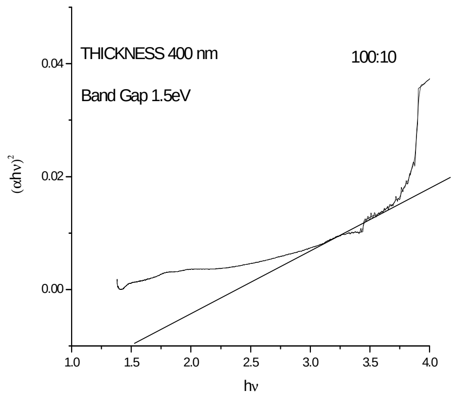


Fig:9 (b)

Fig:9(a) and 9(b) Band Gap of ZnTe: MgPc-90:10mg TF and 100:10mg TF

Fig.9(a) and 9(b) shows the decrease in band gap with change in concentration of ZnTe. Zinc Telluride has a direct band gap of 2.26 eV and Magnesium Phthalocyanine has a band gap 2.6 eV at room temperature. It is observed that the band gap decreases from 2.6 eV to 1.5 eV with increase in concentration of ZnTe.

CONCLUSION

Pure ZnTe and MgPc thin films and their hybrid ZnTe:MgPc thin films with different ratios were coated by thermal evaporation method. The prepared films were annealed at 150^0c and it enhanced the absorption and photoconductivity. The hybrid thin films absorbed almost the entire range of visible light and its absorption increased with the increasing concentration of ZnTe. The photoconductivity increased with increasing concentration of ZnTe in the hybrid thin film. The temperature dependent conductivity of the hybrid thin films indicated exponential behavior of temperature dependent current, confirming the semi-conducting nature of the samples. From the graph of lnI vs 1/KT plots for all the five samples, the activation energy was found out. Activation energy is found to decrease with increasing ZnTe concentration. The thickness of the films ranged between 300nm to 400nm. The band gap of the films calculated ranged between 2.2eV to 1.5eV.

Thus ZnTe plays an enhancing role in the hybrid film of ZnTe/MgPc as an effective photoconductor and as it is shown to be effective photoconductor, the hybrid thin films could be an excellent candidate to be a solar-cell material.

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