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Structural investigation of thermal evaporated Magnesium Phthalocyanine (Mgpc) thin films

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ABSTRACT

Thin films of magnesium phthalocyanine (MgPc) were coated on to glass substrates by thermal evaporation technique. The powder X-ray diffractogram indicated that MgPc crystallizes in monoclinic system with cell parameters 14.368 Å, 4.898Å, β = 119.86^0 with unit cell volume of 1153Å ^{3}. The average volume occupied by a molecule is 288Å^3. The characteristic peak of phthalocyanine (MgPc) is found at 2θ = 7.84 with the hkl value of (100) for both MgPc powder and annealed thin film. The as deposited film was highly amorphous than the annealed film, because the presence of phthalocyanine crystallite form is observed in β-form. The surface morphology of the films annealed at 150^{0}C for 1 hour showed more uniform sized grains than those prepared at room temperature. UV-Visible absorption spectra of pure MgPc thin film, annealed at different temperatures and time duration for annealing were studied. Linear increase in dark and photocurrent was observed for the films annealed at 150^0 C for 1 hour. The variation of band gap energy with different annealing temperature for pure MgPc thin films were studied and the results are tabulated.

Keywords: Photoconductivity, Thin film, Annealing, Solar cell materials, Organic photoconductors, Thermal evaporation.

INTRODUCTION

Phthalocyanines are well known commercial blue-green pigments [1]. Phthalocyanines are class of organic semiconductors which are chemically and thermally stable [2]. Semiconducting properties of phthalocyanines were first observed by Eley [3]. Magnesium Phthalocyanine (MgPc) is a P-type semiconductor with a band gap of 2.6 eV [4], 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 [5].

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 thermal evaporation technique. This method has the advantage of producing high purity films [6].

MATERIALS AND METHODS

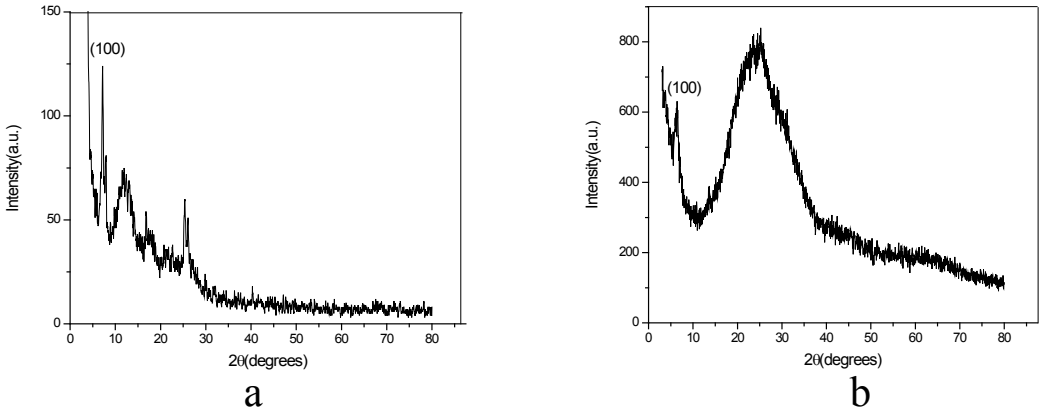
Pure MgPc powder purchased from Aldrich was sublimed in vacuum (Hind Hivac 12 A4-D) at a pressure of 10^{-5} Torr. Glass substrates used were first cleaned thoroughly with liquid detergent; then washed with distilled water; and agitated ultrasonically in acetone. Finally the substrates were dried in 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 DISCISSION

X-ray diffraction analysis

Figure 1(a) shows the X-ray diffractogram profile of pure MgPc in the powder form. In general, a series of crystalline peaks are attributed to polycrystalline nature of MgPc. The characteristic peak of phthalocyanine (MgPc) was found

at 2θ = 7.84 with the hkl value of (100). This is in good agreement with the earlier reported findings elsewhere [8]. The Figure 1 (b) shows the MgPc thin films annealed at 150^{0}C for one hour.



MgPc as-deposited thin film was observed to be amorphous in nature. Higher substrate temperature (75^{0}C -160^{0}C) makes the film crystalline, but the film annealed at 200^{0}C was found to be again amorphous in nature [7]. The XRD pattern showed that MgPc crystallizes in monoclinic system with cell parameters 14.368 Å, 4.898Å, β=119.86^0 with unit cell volume of 1153Å ^{3}. The average volume occupied by a molecule is 288Å^3.

Figure 1- (a) XRD of Pure MgPc powder and 1 (b) MgPc thin film annealed at 150^{0}C for 1 hour.

While comparing the as-deposited and annealed MgPc films, it is found that the as deposited film is highly amorphous than the annealed film, because the presence of phthalocyanine crystallite form is observed in β-form. The β-form is not perfectly visible in the as deposited film, whereas it is evidently seen in the annealed thin film.

Sem analysis

The Scanning Electron Microscope (SEM) images have a characteristic three-dimensional appearance and are useful for studying the surface structure of the coated area. The morphology of the prepared films, after thermal treatment, has been investigated by SEM.

The surface morphology of the films deposited at room temperature has appeared to be non-uniform with smaller grains and exhibits a coarse structure. Annealing of the films favors growth and agglomeration of small grains. The SEM analysis of Pure MgPc thin film with different magnification was shown in Figure 2 (a) and (b). The films annealed at 150^{0}C for 1 hour showed more uniform sized grains than those prepared at room temperature. In the annealed films, the surface is dense, smooth and no pinholes were observed. Further, increase in annealing causes significant modification in the surface. From the surface analysis, it was found that the films exhibit uniform thickness.

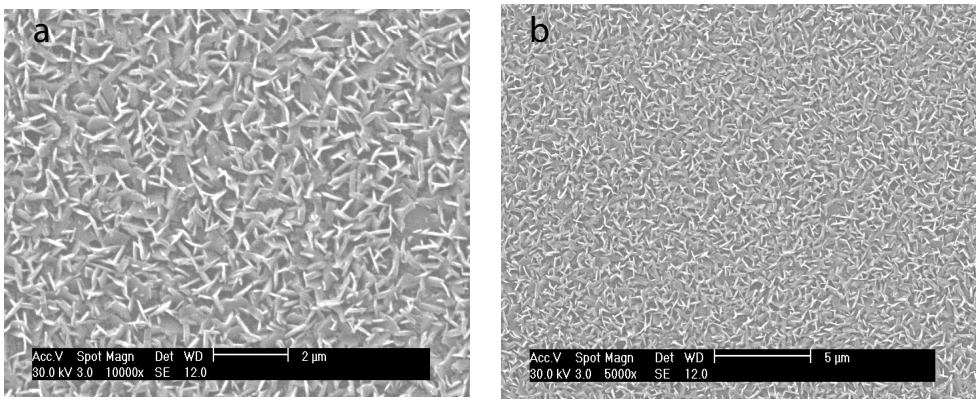


Figure 2- (a) and (b) SEM of Pure MgPc thin film with different magnification.

Optical studies

The UV-Visible absorption spectra for the sample was recorded in the range 250-1200 nm. The absorption spectra of pure magnesium phthalocyanine thin film, annealed at different temperatures and time duration for annealing were studied. From the spectra, it was found that the absorption increases with increase in annealing temperature up to 150^{0}c. Further increase in annealing temperature results in decrease in absorption as could be gathered from Figure 3 (a) and (b).

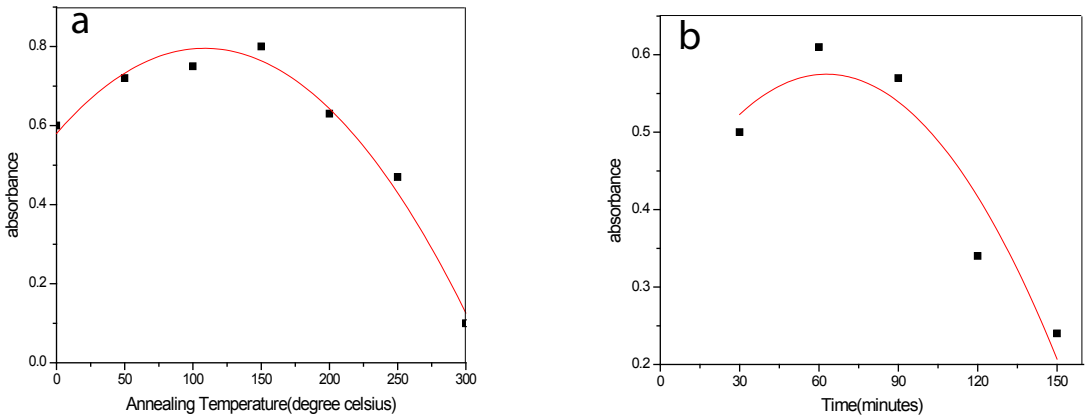


Figure 3 - (a) Annealing temperature vs absorption and 3 (b) Absorption vs annealing temperature 150^{0}C with different timings for pure MgPc thin film

Figure 4 shows the absorption spectra of pure MgPc thin films air annealed at 150°C. It is observed that the thin film has a very wide absorption range over the visible region with significant peaks at 650 nm and 700 nm for MgPc. The air annealed film has better absorption when compared with as-deposited thin film. The band gap of pure MgPc thin film was obtained from the absorption spectra using Tauc's plot.

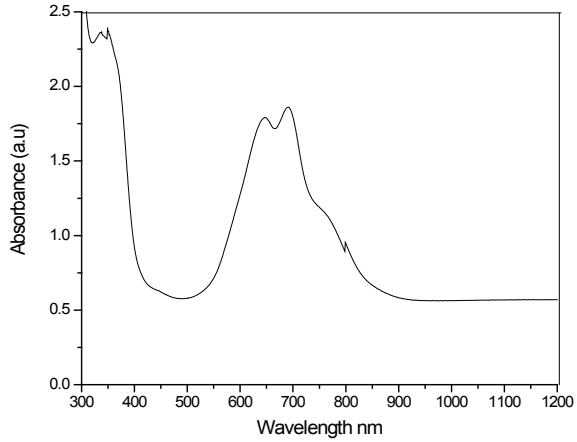


Figure 4 - Absorption spectra of pure MgPc thin film air annealed at 150°C for 1 hr.

Table 1 shows the variation of band gap energy with different annealing temperature for pure magnesium phthalocyanine thin films. From the table it is observed that as the annealing temperature increases, the band gap decreases up to 150^{0}C. But beyond 150^{0}C, the band gap increases for the prepared thin films.

Table-1: Variation of Band Gap energy with Annealing Temperature for pure MgPc thin films.

Annealing Temperature (degree Celsius)	MgPc Thin film Band Gap (eV)
30	2.76
50	2.74
100	2.72
150	2.69
200	2.73
250	2.81

Photoconductivity studies

The plots indicate linear increase of current in dark and when illuminated by visible light using 100W halogen lamp. This is because of the capability of MgPc to absorb in the visible region of 550-800 nm respectively (Figure 5).

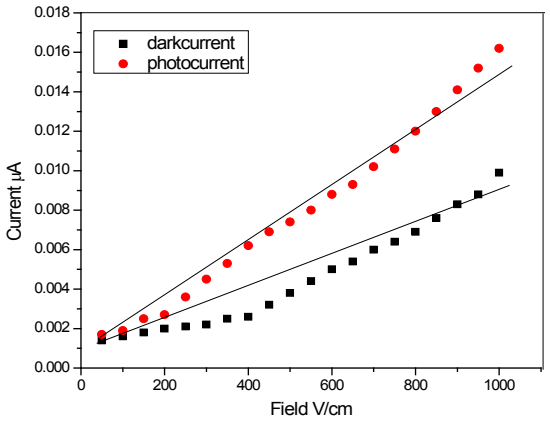


Figure 5 - Field dependent dark and photoconductivity for (a) pure ZnTe and (b) pure MgPc Thin film annealed at 150^{o}C for 1 hr.

CONCLUSION

Pure magnesium thin films were prepared using thermal evaporation technique. The XRD studies confirmed the amorphous nature of the as-deposited films, because the presence of phthalocyanine crystallite form is observed in β-form. The β-form was not perfectly visible in the as deposited film, whereas it was evidently seen in the annealed thin film. For films annealed at 150^{0} C for 1 hour, wide absorption was obtained and linear increase in photocurrent was observed. The band gap of MgPc was found to be 2.6 eV. The surface of the film was smooth and coated uniformly without pin holes and grain boundaries. Thus the prepared thin film could be a better photoconductor for solar cell applications.

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