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Electrical and Optical Characterization of Vacuum Evaporated Magnesium Phthalocyanine Thin Films

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The electrical and optical characterization of magnesium phthalocyanine films has been made. The activation energy has been obtained. Optical spectra of as deposited and air annealed films are reported. The optical band gap is obtained as 2.6 eV.

INTRODUCTION

There is considerable interest in the metallophthalocyanines as industrial dyes, as potential photosensitizers in the conversion of solar energy to chemical or electrochemical energy, for use in photodynamic treatment of cancer, and as sensors for the quantitative detection of atmospheric pollutants (1, 2).

Most phthalocyanine compounds are insoluble in common organic solvents and so it is not possible to prepare them by solution casting techniques. Hence, very often, thin films of phthalocyanines are made by a vacuum evaporation technique. This method has the advantage of producing high purity films.

EXPERIMENT

Thin films of magnesium phthalocyanine (MgPc) are prepared by the vacuum evaporation technique using a Hind Hivac 12A coating unit on to well cleaned microscope glass slides held at a pressure of 10^{-5} Pa. The resistive heating element is a molybdenum boat of dimensions $2.9 \times 1.2 \times 0.009$ cm. The thickness of the film is determined by the Tolansky technique (3). Using monochromatic light from a sodium vapor lamp the arrangement produces the interference pattern for the Fizeau fringes.

Conductivity studies have been done using the programable Keithley electrometer (Model No. 617) and a conductivity cell. The conductivity measurements are performed in the temperature range 300–460 K in vacuum. Evaporated silver electrodes are used as ohmic contacts. The temperature is monitored using a copper-constantan thermocouple attached to the substrate. Optical studies have been done using the spectrophotometer Shimadzu 160A.

RESULTS AND DISCUSSION

The core structure of the phthalocyanine macrocycle is formed by four isoindole units endowing the molecule with a two-dimensional conjugated (π)-electron system. A schematic diagram showing the molecular structure of MgPc is shown in Fig. 1. The physical and chemical properties of phthalocyanines can be altered by incorporating different metal atoms at the center of the macrocycle and by substituting the periphery with a variety of functional groups. Here magnesium is the central metal and there are no periphery substitutions. Electrical studies aimed to calculate the activation energy and determine the type of conductivity. Studies were done using the standard two probe method under rotatory vacuum (10^{-3} Pa) to prevent any type of contamination. Resistence is measured at intervals of 5 K. Arrhenius plots for as deposited films of different thicknesses are shown in Fig. 2. The slope of the graph is used to obtain the activation energy (E) from the formula

$$\sigma = \sigma_0 \, e^{(-\Delta E/kT)}.$$

σ is the conductivity of the film, k is Boltzmann constant, and T is the temperature in absolute scale. It is observed that as the thickness of the film increases, activation energy increases. For thicknesses 571, 843 and 855 nm the activation energies obtained are 0.023, 0.031, and 0.033 eV, respectively. The hot probe method confirmed the conductivity to be p-type.

The optical density spectra of the sample were obtained from 200 to 1100 nm. The features of the spectrum for as deposited film are (i) high absorption is in the UV region (250–400 nm) with a λ_{maximum} at 365 nm and from yellow to near IR (550–850 nm) and (ii) high transmission from violet

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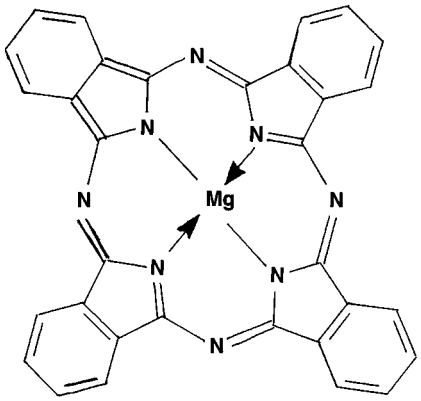

FIG. 1. Schematic diagram of the molecular structure of MgPc.

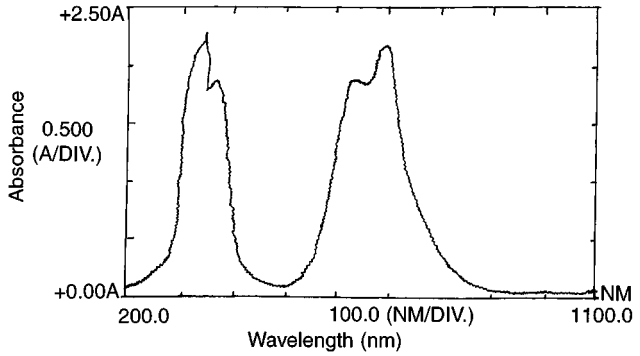

FIG. 3. Optical absorption spectra of as deposited MgPc thin films.

to green (400–550 nm). The spectrum shows an intense absorption maximum at about 693 nm with a shoulder around 632 nm and is given in Fig. 3. Figure 4 gives the optical spectra for films annealed in air for 24 h at 125°C. The maximum absorption is shifted to 333 nm.

The UV–visible spectrum observed for phthalocyanines originates from molecular orbitals within the aromatic 18 π electron system and from overlapping orbitals on the central metal (4). Here the Q band (500–750 nm) and the B band (250–400 nm) are well separated. The characteristic optical spectrum is dominated by allowed π–π^* transitions. The spectral envelope in the B region is dominated by a transition to nondegenerate states as well. On annealing the film we have seen from Fig. 4 that there is considerable broadening of the Q and B bands. In recent years there has been an interest in extending the absorption band of phthalocyanines into the near infrared region of the spectrum for a range of potential functional applications including optical data storage and security printing (5).

Geometry of the spectrophotometer is so adjusted at normal incidence that the reflectance from the sample is zero. Hence using the equation $\alpha = 2.303\,A/t$, where α is the absorption coefficient, A the absorbance, and t the thickness of the film, the direct band gap is estimated using the relation

$$\alpha \sim (hv - Eg)^{1/2}.$$

Here Eg is the optical band gap and hv is the photon of energy. By plotting α^2 versus hv and extrapolating to zero absorption, Eg is obtained as 2.6 eV for the as deposited sample, as shown in Fig. 5. The band gap does not show any remarkable difference from its value in the case of the air annealed sample.

CONCLUSION

The electrical conductivity studies and activation energies of evaporated MgPc thin films have been made using ohmic silver electrodes. The activation energy is found to be

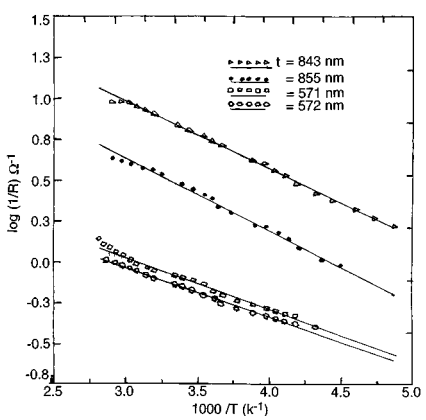

FIG. 2. Plot of $\log 1/R$ Versus $1000/T$.

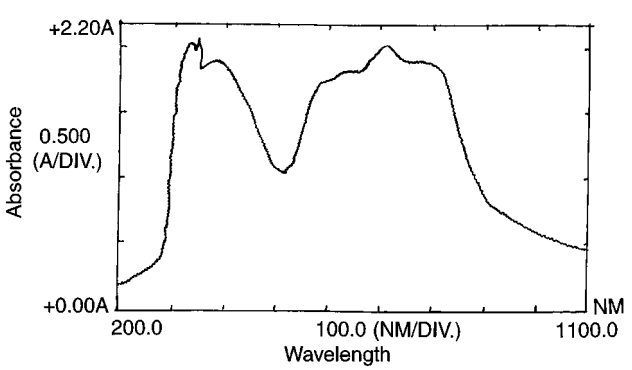

FIG. 4. Optical absorption spectra of annealed MgPc thin films.

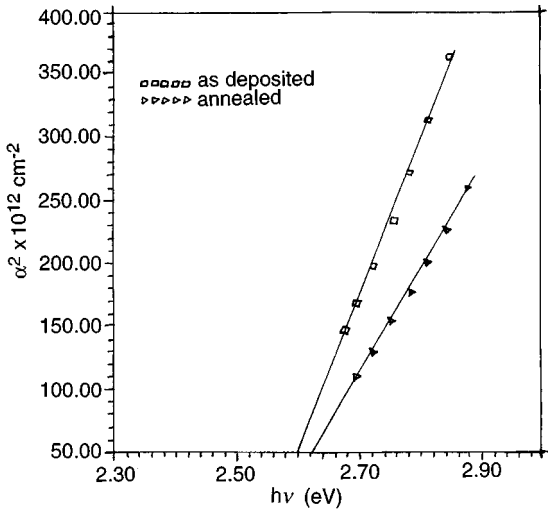

FIG. 5. Plot of α^2 Versus $h\nu$.

0.033 eV for films of thickness 855 nm. The absorption spectrum of the as deposited samples yields a band gap of 2.6 eV. The spectrum shows that MgPc can be used as a selective optical absorption coating in the visible region at room temperature.

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