Copper phthalocyanine films for photovoltaic applications

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Hot wall technique has been used to grow a series of copper phthalocyanine (CuPc) films. These samples have been studied for their structural, optical and electrical properties. The X-ray diffraction and SEM pattern of these films show crystalline behaviour of films. The electrical conductivity and optical band gap of the films increase with increase in substrate temperature, whereas activation energy decreases. The activation energy of the films is found to lie in the range 0.45-0.55 eV. Analysis of optical absorption measurements on the films indicates that the interband transitions energies lie in the range 2.3-2.55 eV. Keeping in view, the electrical and optical properties of CuPc films single layer (fluorine doped tin oxide/CuPc/aluminium) and double layer (fluorine doped tin oxide/crystal violet/CuPc/aluminium) junctions have been fabricated under different experimental conditions. The J-V relationship for the single and double layer devices are found to be in good agreement with standard diode equation.

Keywords: Evaporation, Copper phthalocyanine, Scanning electron microscopy, X-ray diffraction, Electrical properties, Optical properties, Photovoltaic devices

1 Introduction
The metal substituted phthalocyanines have attracted significant interest in last few years due to their photosemiconducting and optical properties. They are used in photocopiers, laser printers, optical data storage systems, solar cells, fuel cells and gas sensing systems. Thin films of copper, zinc, nickel and cobalt substituted phthalocyanines have been extensively studied by different researchers. Copper phthalocyanine has attracted considerable interest because of its outstanding optical and electrical properties, which may open a wide variety of potential applications in modern optical recording and optoelectronic devices.

In this paper, the synthesis, structural, electrical and optical properties of copper phthalocyanine (Fig. 1) films prepared by hot wall technique onto the glass substrate kept at different temperatures has been studied. Also, current density-voltage (J-V) characteristics of single and double layer devices based on CuPc have been reported.

2 Experimental Details
The copper phthalocyanine powder was taken in a single-evaporation zone hot wall set-up. The whole apparatus was fitted onto the base plate of the vacuum chamber of Hind High Vacuum coating unit 12A4H. The chamber was then evacuated to pressure of order less than 10⁻⁵ Torr after mounting the substrate and making other desired adjustments. After attaining the desired experimental conditions, the source heater was switched on and the substrate holder was positioned on the top of the tube to make it a closed system. For fabrication of devices, CuPc films were deposited on the fluorine doped tin oxide (FTO) coated glass substrates by hot wall technique.

The thickness of the films was measured by using depth profiler (Dektek 3030-XT). The IR spectra of

Fig. 1—CuPc molecule
the samples were taken using a Fourier transform infrared spectrophotometer (FTIR-8400S). $^1$H Nuclear Magnetic Resonance spectra have been recorded on Bruker AC 200 MHz machine. The surface morphology of copper phthalocyanine films were studied by JEOL JSM-6100 (Japan) scanning electron microscope. The XRD scans of films were taken using CuK$_\alpha$ radiation in the 2θ range 0-40° by Philips diffractometer. The transmittance spectra of the samples were obtained in the photo energy range 1.12-4.13 eV by using UV-1601PC (Shimadzu, Japan) spectrophotometer. The electrical resistivity of CuPc films were determined using two probe technique in the temperature range 290-400 K under a pressure of $10^{-4}$ Torr.

3 Results and Discussion

The thickness of CuPc films prepared at different substrate temperatures lies between 100-110 nm. The comparison of FTIR spectra of copper phthalocyanine and corresponding film, shows that the compound remains unaffected during vacuum deposition and annealing processes because of unchanged vibrational frequencies (cm$^{-1}$).

The SEM image of CuPc films (Fig. 2) depicts a unique microstructure with crystallites aligning in the direction nearly perpendicular to substrate plane. On average, long crystallites as wide as 1 μm are noticed in case of films deposited at 423 K. An appreciable increase in crystallite size has been noticed with increase in substrate temperature. The X-ray diffractogram obtained for CuPc films shows the presence of a sharp and well resolved diffraction peak, which confirms its crystalline behaviour. The films deposited at higher substrate temperature show comparatively intense diffraction peaks. Moreover, a decrease in full width measured at half maxima (FWHM) of diffraction peaks has been noticed, thus suggesting a higher degree of crystallinity and increase in particle size.

Fig. 3 shows the plots of temperature dependence of electrical resistivity for the CuPc films. Observations reveal that, the resistivity of the films decreases with increase in temperature, within the experimental range (290-400 K). The temperature dependence of log $\rho$ shows almost straight line, indicating the applicability of well-known Arrhenius relation $\rho = \rho_0 \exp (\Delta E/2kT)$ for these films, where $E$ is the activation energy and is found to lie in the range 0.45-0.55 eV. It has also been observed that the electrical resistivity and activation energy of films decrease with increase in the substrate temperature, which may be explained using Petritz’s barrier model. Since the crystallites do not grow sufficiently large at low temperatures, the inter-crystalline regions are wide, offering a high resistance to the movement of charge carriers. The formation of fewer nucleation centres at higher substrate temperatures results in large crystallites, which ultimately decrease the barrier size. The charge carriers have to cross narrow inter-crystalline barriers and therefore may cause decrease in resistivity and activation energy.

The optical band gap energy has been determined from the absorption coefficient of CuPc films over the fundamental absorption edge. From the curve fittings, it has been found that the direct interband transition takes place in these samples and obey the formula.

![Fig. 2—SEM micrographs for CuPc films deposited at 423 K.](image)

![Fig. 3—Temperature dependence of log of resistivity of CuPc films deposited at (I) 323 K, (II) 373 K and (III) 423 K.](image)
Fig. 4—Spectral variation of absorption coefficient for CuPc films deposited at (I) 323 K, (II) 373 K and (III) 423 K.

\[ \alpha(h\nu) = B(h\nu - E_g)^{1/2} \]

where \( E_g \) is the band gap. The plot of the square of the absorption coefficient versus photon energy, of the films prepared at different temperatures is shown in Fig. 4. The extrapolation of the straight lines to \( \alpha h\nu = 0 \), gives the values of optical band gap and is found to lie in the range 2.3-2.55 eV for CuPc films. This increase in the optical band gap energies of CuPc films with substrate temperature may be due to the fact that, films deposited at higher substrate temperatures favour the growth of larger grain sizes with high degree of orientation of grains, which provides less contribution to absorption.

Keeping in view, the electrical and optical properties, CuPc films deposited at 423 K have been selected for the fabrication of single layer (FTO/CuPc/Al) and double layer (FTO/CuPc/Crystal violet/In) devices. Figs 5(a) and 6(a) show the steady state current density-voltage \((J-V)\) characteristics of single and double layer devices in dark. These \(J-V\) characteristics results are in agreement with standard diode equation

\[ J = J_0 \left[ \exp(qV/nkT) - 1 \right] \]

The \( J-V \) characteristics of single and double layer devices under illumination are shown in Figs 5(b) and 6(b). The typical parameters such as open circuit voltage \((V_{oc})\), short circuit current \((J_{sc})\), and fill factor \((FF)\) have been calculated from the \(J-V\) plots under illumination and are reported in Table 1. It is found that double layer device show larger value of \(J_{sc}\) and lesser value of \(V_{oc}\), which confirm that photoinduced electrons and holes are efficiently separated within the interface and collected by the contact electrodes. Moreover, the fill factor of double layer device found to be increased by nearly three times than single layer device. Also, here fill factor of 0.56 represents some improvement as compared to earlier studied CuPc based photovoltaic devices.
4 Conclusions

Hot wall technique is found to produce well ordered and conducting CuPc films. The substrate temperature appears to be important parameters for molecular packing in the solid state structure and influence the properties of the CuPc films. The $J-V$ relationship for the single and double layer devices are found to be in good agreement with standard diode equation. It is found that double layer devices are more efficient than single layer devices based on CuPc.

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References