Synthesis and UV-Visible Characterization Study of Spin Coated Copper Phthalocyanine Films

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Abstract

Copper phthalocyanine in powder form is synthesized in the laboratory using phthalic unhydride and urea route by chemical method. Spin coated Copper phthalocyanine films are constructed used to study UV-Visible characterization spectra. The energy band gap is determined from UV-Vis spectra. Present results shows the existence of direct allowed energy gap at 2.6 eV for the films before and after annealing These values are calculated at the intense band called the Soret band which is characteristics of metallophthalocyanines. The energy gap is estimated to be 1.6 eV for pristine film and 1.7 eV for annealed film.

Key Words: Copper phthalocyanine, spin coating, band gap

Introduction:

Recently there has been a considerable interest in exploiting organic substances such as metallophthalocyanines (MPcs), porphyrins, and doped conducting polymers. For getting higher surface area and maximum sensing these materials are suited in the form of thin or thick films. MPc is a well known material because of its extensive applications in different areas [1]. They possess electronic and morphologic characteristics which are very favorable for semiconductive properties. The resistance of a device varies by exposure to chemical substance. Moreover MPcs have high thermal and chemical stabilities [2]. Copper phthalocyanine is synthesized and films are formed on the glass substrate using spin coating method.

Experimental:

Various methods for synthesis of MPcs are reported in the literature as mentioned in chapter 2, from which the one with phthalic anhydride and urea method was selected. The phthalic anhydride-urea method was simple and can be easily carried out in the present laboratory [3]. The synthesis of copper phthalocyanine, cobalt phthalocyanine, nickel phthalocyanine, zinc phthalocyanine, iron phthalocyanine, aluminum phthalocyanine, cadmium phthalocyanine, lead phthalocyanine, silver phthalocyanine were carried out using this route. The reaction scheme of this synthesis method [4] is shown in Figure 1.

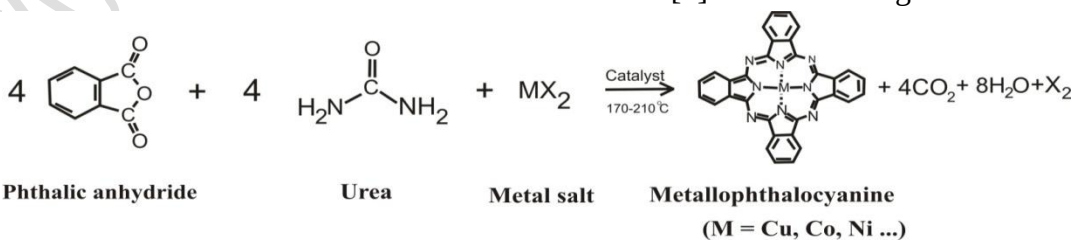

Figure 1: Reaction scheme used in the preparation of the metallophthalocyanines

Synthesis procedure [5] involves mixing of phthalic anhydride, urea and metal salt along with the catalyst ammonium molybdate. Phthalic anhydride, urea and metal salts were taken in the weight proportion of 4:4:1. Ammonium molybdate is used for synthesis of each MPc. These precursors were crushed together and mixed properly. The mixture was then heated with constant stirring. In the first step, slurry of the mixture was obtained, continuing heating of the slurry, the cyclotetramerisation reaction took place and it was observed to be very vigorous. Reaction took place at about 200°C - 250°C and colour change of the product was observed, after completion of the reaction. The residue was crushed to a fine powder and washed with methyl alcohol more than 20 times and with distilled water several times for purification so that unreacted precursors were removed. The powder was then air-dried under IR lamp and uniformly crushed to make fine and uniform granules of powder. Films of CuPc have been fabricated by spin coating technique on glass substrate at room temperature. The CuPc solution in chlorobenzene and TFAA was used to fabricate the film. After deposition the films were annealed at 150°C temperature for 2 hours.

The UV-visible absorption spectra have been measured and energy gap is estimated for the CuPc solution, the spin coated pristine films and spin coated annealed films. The optical properties were studied to determine the crystal phase because the optical properties of these materials are dependent on the crystal phases and its structure [6,7]. The knowledge of phase morphology will help to compare the gas sensing properties of different phases.

Result and Discussion:

Figure 2 shows the absorption spectra of CuPc solution in chlorobenzene and TFAA.

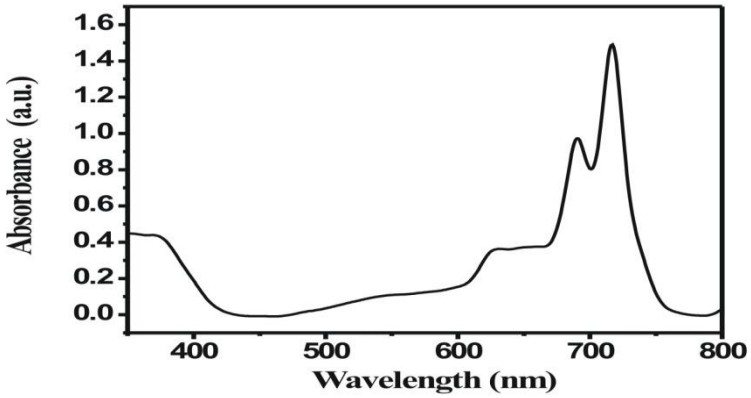

Figure 2: The absorption spectra for CuPc solution in chlorobenzene and TFAA

The UV-visible absorption spectra of spin coated films are shown in Figure 2. Figure shows spectra of both pristine and annealed films. Two absorption maxima are seen at the Q band with wavelengths of 623 nm and 697 nm. The two maxima peaks are separated by 74 nm. The intensity of the higher energy peak is larger than that of the second peak. This behavior indicates the α-phase of CuPc [8]. UV-Visible spectra

indicates that the spin coated annealed film (150°C) shows large intensity of the higher energy peak than that of the second peak. This typical behavior is of α-phase morphology. Hence the CuPc film prepared in the laboratory using spin coating technique and annealed at 150°C is having α-phase morphology.

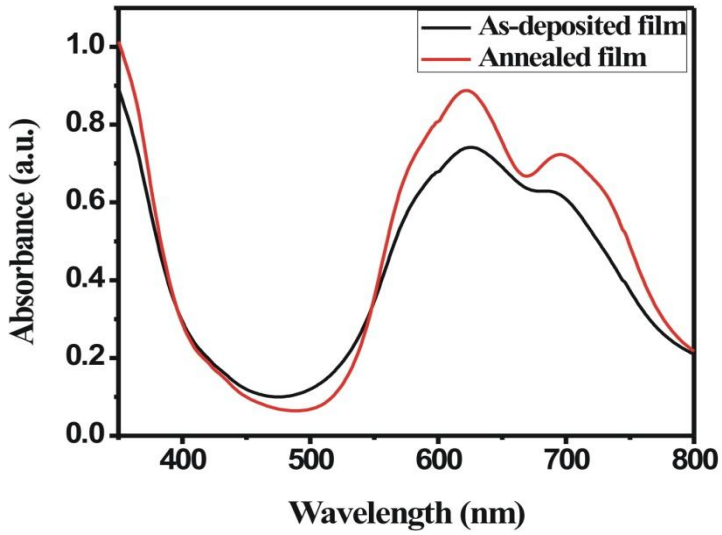

Figure 3: Absorption spectra of pristine and annealed spin coated CuPc films

The direct allowed band gap energy is determined by plotting α^2 as a function of photon energy hν as shown in figure 4 and 5. Optical band gap is determined from the analysis of the spectral dependence of the absorption near the fundamental absorption edge. Present results shows the existence of direct allowed energy gap at 2.6 eV for the films before and after annealing which is in agreement with the literature [9, 10]. These values are calculated at the intense band called the Soret band which is characteristics of metallophthalocyanines. The energy gap is estimated to be 1.6 eV for pristine film and 1.7 eV for annealed film.

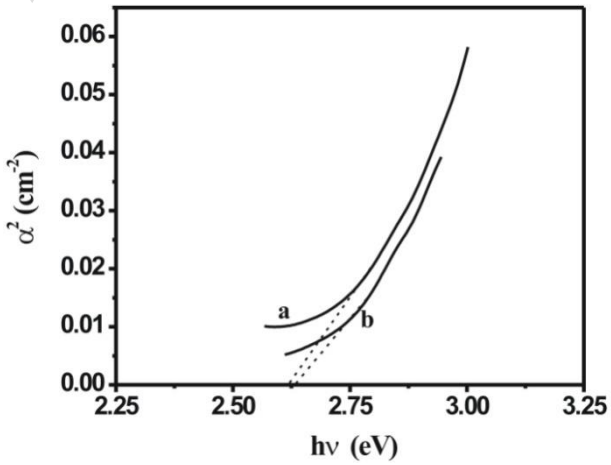

Figure 4: The plot of α^2 versus hν for CuPc spin coated a) pristine and b) annealed films

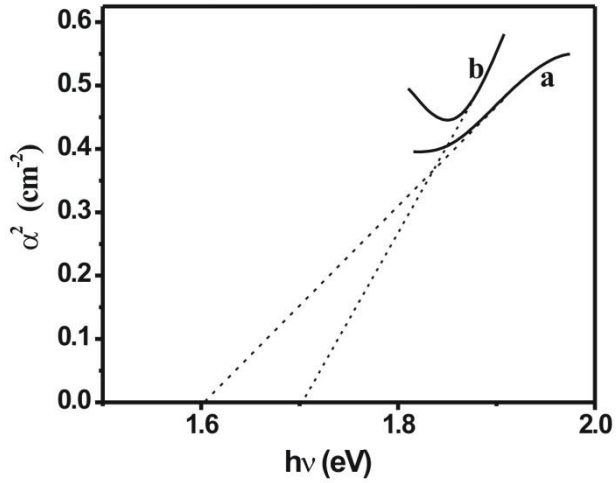

Figure 5: The plot of α^2 versus hν for CuPc spin coated a) pristine and b) annealed films

The stability in the peak positions in the absorbing region of absorption spectra of pristine and annealed films show the stability of the structure of CuPc. The absorption spectra occur in the high energy region of the soret band indicates the presence of 'd' band associated with the central metal atom. It is thought that π-d transitions are involved because CuPc has partially occupied d band. The results also show that there is no effect of the annealing on the optical properties of CuPc films upto annealing temperature of 150ºC. Higher temperature annealing produces the transition from one phase to another. The variation in band gap energy for CuPc is marked which can be attributed to a phase change for CuPc between 150°C and 200°C [11].

It is in good agreement with the results of absorption spectra change observed due to heat treatment for CoPc [12]. The film deposited at room temperature is identified to be of α-form and the complete phase change is reported around 300°C [13]. Hence to use the films for gas sensing applications, the annealing was done at lower temperature than 210°C, preferably at 150°C.

Conclusion:

Existence of direct allowed energy gap at 2.6 eV for the films before and after annealing these values are calculated at the intense band called the Soret band which is characteristics of metallophthalocyanines. The energy gap is estimated to be 1.6 eV for pristine film and 1.7 eV for annealed film. Hence to use the films for gas sensing applications, the annealing was done at lower temperature than 210°C, preferably at 150°C.

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