Effect of γ-radiation on the Conduction Mechanism of Thermal Vacuum Deposited Copper Phthalocyanine Thin Films

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Abstract

The dosimetry properties of thermally evaporated Copper Phthalocyanine (CuPc) thin films were investigated. The conduction mechanism of the as-deposited films was found to be space-charge-limited and their relative permittivity was within the range reported by others [1, 2, 3, 4]. The Poole-Frenkel effect became more dominant for the irradiated samples and they displayed large increase in permittivity and colour centre density, although the energies of their optical band gap and trapping levels did not change. The observed linear relationship between the absorbance at 615 nm and the γ-radiation doses validated the use of CuPc as an optical sensor dosimeter especially for low radiation doses. Samples showed a higher radiation tolerance after being annealed for one hour at a temperature of only 323 K. Annealing also restored their initial electrical and optical properties.

1. Introduction

The objective of this study was to explore the use of CuPc as an ionising radiation detection material. CuPc is a p-type semiconductor with a large energy band gap [5, 6]. Investigations were based on the exploitation of radiation-induced structural defects (known as colour centres) that are formed when an electron becomes bound to a vacancy. Colour centres density increases on exposure to γ-rays and this changes the material's optical absorption bands and electrical conduction mechanism [7, 8, 9, 10].

2. Experimental procedure

Thin films of CuPc were deposited on suitably prepared glass substrates using an Edwards E306A thermal coating system, which was initially evacuated to a partial pressure of $2x10^{-6}$ mbar. The substrate temperature was 373 K. Thin films of 190 nm in thickness were deposited by evaporating CuPc powder from a tungsten boat under a vapour pressure of $6x10^{-5}$ mbar, at a deposition rate of 2-3 nm/s. Thin film Aluminium contacts of 100 nm in thickness were deposited so that Al/CuPc/Al devices were formed in an MIM (Metal-Insulator-Metal) configuration, with an active area of 2.5 cm X 2.5 cm. The UV/Visible spectra were recorded for as-deposited and irradiated samples at room temperature using a Varian DMS-100S UV-visible spectrometer. Samples were independently exposed to doses of γ-radiation (180 Gy-1080 Gy) from a ^{60}Co source at a dose rate of 6.0 Gy/min. They were later annealed at a temperature of 323 K, under a pressure of 10^{-3} mbar.

3. Results and Discussion:

3.1. Effect of γ-Radiation on the Optical Properties of CuPc Thin Film

The obtained UV/Visible absorbance spectra for both the as-deposited and irradiated CuPc thin films (Figure 1) are believed to result from the interaction of the ultraviolet and visible light with molecular orbitals in the 18π configuration and also from the overlapping of electronic orbitals on the central copper atom [11].
The direct allowed electronic transition occurs between the $\pi \rightarrow \pi^*$ orbitals [12, 13, 14]. Such a transition is exhibited by an absorption band known as the B-band in the 290-430 nm region. This transition yields the absorption edge values. The energies of the two trapping centres are obtained from the Q-band region (490-800 nm). The values of the optical band gap and trapping levels are obtained in view of Mott and Davis' model [15] for the direct allowed transition as follows:

$$\alpha(\nu)\, h\nu = B\,(h\nu - E_{opt})^{1/2} \qquad (1)$$

E_{opt} is the optical energy band gap, ν is the frequency of the incident photons, B is a constant obtained from the slope of the $(\alpha h\nu)^2$ versus hν (Figure 2) and the absorption coefficient $\alpha(\nu) = 2.303\ A/d$, where A is the absorbance and d is the film thickness. Figure 2 shows plots of $(\alpha h\nu)^2$ versus hν for the as-deposited and irradiated films. The extrapolations of the straight lines

(where $(\alpha h\nu)^2 = 0$) yields a value of 3.26 eV for the absorption edge and the values of 1.66 eV and1.89 eV for trapping levels for the as-deposited samples.

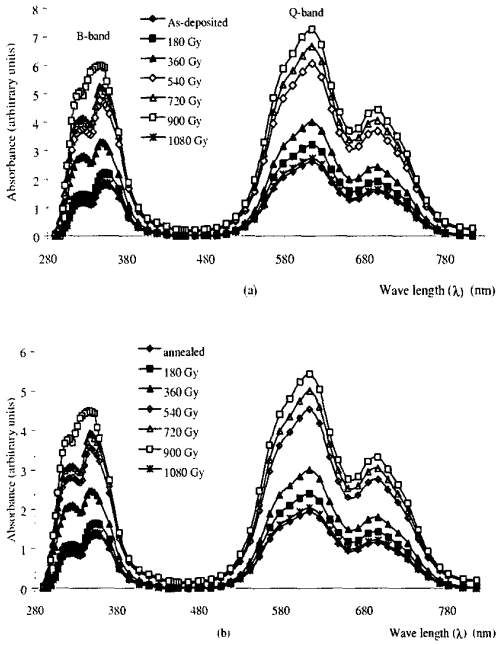

Figure 1. *UV-Visible absorbance spectra for CuPc thin films illustrating the effects of γ-radiation on the B and Q absorbance bands of (a) the as-deposited and (b) the annealed samples.*

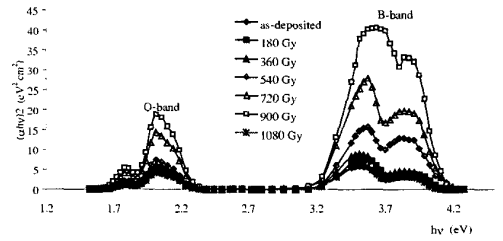

Figure 2. *extrapolation of $(\alpha h\nu)^2$ versus $h\nu$ for the as-deposited and irradiated CuPc thin films; the absorption edge is obtained at the B-band and the trapping levels at the Q-band.*

The energy of the absorption edge and trapping levels remained unaffected by exposure to γ-rays. The values for the as-deposited samples were higher than those reported by Ambily and Menon [13]. This may be attributed to the difference in P/R (the ratio of the deposition rate and chamber pressures).

3.2. Effect of γ-radiation on the Colour Centre Density of CuPc

The charge carrier concentration or the colour centre density can be estimated by using Smakula's equation [7]:

$$N_f = 0.89x10^{17}\, uwn_i/(n_i^2 + 2)^2 \qquad (2)$$

N_f is the charge carrier concentration or the colour centre density, f is the oscillator strength which is assumed to be unity, u is the full width at half maximum (FWHM) of the absorption band of the optical spectra and w is the absorption coefficient at the centre of the absorption band. The refractive indices (n_i) were obtained from the dielectric constant measurements for the MIM devices using an impedance analyser (hp 4277A LCZ-meter):

$$\epsilon_r = Cd/(\epsilon_o A) \qquad (3)$$

$$n_i = (\epsilon_r)^{1/2} \qquad (4)$$

Where ϵ_r and ϵ_o are the relative permittivity and the permittivity of free space respectively, d is the thin film thickness, A is the effective area of the MIM device, C is its measured capacitance and n_i is the refractive index at each radiation dose.

The values of the colour centres density for the irradiated samples showed a significant increase in comparison to the as-deposited until reaching a saturation level of 900 Gy. However, further exposure to γ-rays caused a decline in density of the colour centres. It is believed that as the γ-ray exposure exceeds the saturation level, the interaction of the colour centre components (electron or hole) with γ-ray itself may become a more likely event resulting in the liberation of either electrons or holes from the bound electron-vacancy structure. Consequently, the absorption bands and colour centres density decrease in value for doses above the saturation level.

3.3. Effect of γ- radiation On CuPc Thin Films Conduction Mechanism

Figure 3 shows the curves of current versus voltage for the as-deposited and the irradiated thin films. Clearly the I-V relationships for the irradiated samples are different from those of the as-deposited implying a change in the conduction mechanism. The I-V characteristic curves of the as-deposited films have shown ohmic conduction at low voltages and a space-charge-limited conduction mechanism (SPCLC) at

higher voltages. In particular, the fitting of the I-V curves above 2V yielded power law dependence with an exponent of about 3.5 for the as-deposited samples (Figure 3a). Sussman [1], Hamann [2], Gould [3] and Delcote et al [4] have conducted comprehensive studies into the conduction mechanism of copper phthalocyanine thin films and concluded that the space-charge-limited mechanism provides the dominant means of conduction. However, when the CuPc thin films were irradiated, their I-V curves exhibited a linear to less than quadratic dependence at high fields. In such cases, the SPCLC is no longer apparent.

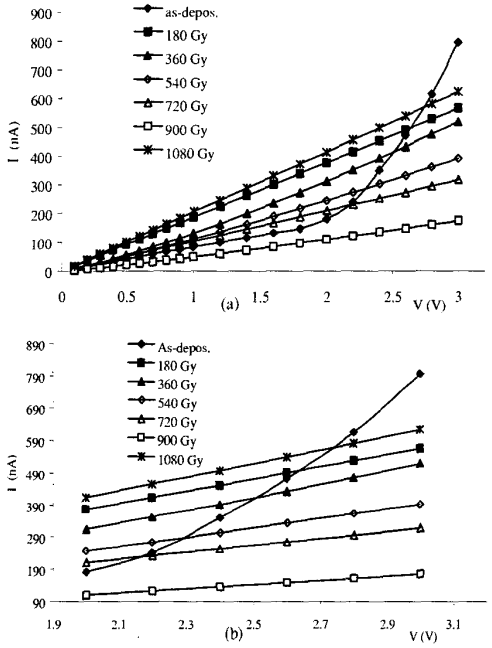

Figure 3. *I-V characteristics for CuPc thin films. (a) The curve of the as-deposited sample shows a linear ohmic behaviour for less than 1.8 V and SPCLC for greater than 1.8 V. The curves of the irradiated samples exhibited a close to linear behaviour. (b) The best fitting lines for the high-field, display an exponent of 3.5 for as-deposited, indicative of SPCLC and less than 2 for irradiated samples, indicative of the absence of SPCLC.*

Further analyses of the irradiated films are presented in Figure 4. In this figure, the log(I) versus $V^{1/2}$ plots are linear, which indicate that they obey either the Schottky emission or the Poole-Frenkel effect. These phenomena are described by:

$$I_C \propto \exp(\beta E^{1/2}/kT) \qquad (5)$$

Where I_C is the circulating current, E is the applied electric field, k is Bolzmann's constant, T is the absolute temperature (K) and β is the high field-lowering coefficient approximated by the slope of log (I) versus $V^{1/2}$ (Figure 4).

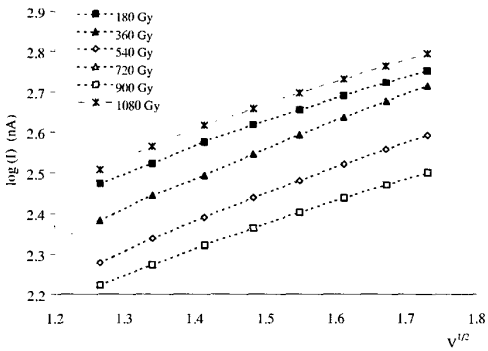

Figure 4. *Log(I)-$V^{1/2}$ for the irradiated CuPc thin films. The linearity shows that they obey Schottky or Poole-Frenkel conduction mechanisms.*

In addition, the permittivity values listed in Table 1 for the CuPc thin films were obtained from either direct measurement using an impedance analyser (HP 4277A LCZ-meter) or estimated using the high-field lowering coefficients as follows:

$$\epsilon_r = e^3/m\pi\epsilon_o\beta^2 \qquad (6)$$

ϵ_o is the free space permittivity, ϵ_r is the material's relative permittivity, e is the electronic charge in coulombs and m = 1 for Poole-Frenkel or m = 4 for the Schottky conduction mechanism [16].

γ-Ray Exposure Dose (Gy)	High-Field Lowering Coefficient $\beta x10^{-5}$ ($eV\ V^{-1/2}cm^{1/2}$)	Permmitivity		
		Measured LCZ-meter	Poole-Frenkel Effect	Schottky Emission
As-depos.	36	4.4	4.4	1.10
180	32	5.0	4.8	0.70
360	30	5.7	5.0	1.10
540	25	6.4	6.1	0.55
720	21	7.4	6.9	1.80
900	18	8.9	6.9	1.60
1080	34	4.8	4.5	1.10

Table 1. *The high-field-lowering coefficient and relative permittivity for the as-deposited and the irradiated samples.*

Both of the directly measured and the estimated Poole-Frenkel relative permittivity values for the as-deposited and annealed Al/CuPc/Al devices vary from 4.2 to 4.4. Such values are within the range (2.4-5.1) reported by other workers [1 - 4, 17].
Gould attributed the wide discrepancy in permittivity to the differences in the chamber pressure and deposition rate (P/R) [4]. When as-deposited CuPc thin films were

exposed to γ-radiation doses above 900 Gy they manifested large deviations in their relative permittivity (5.3-7.6, Table 2). Such values are too large to satisfy Schottky emission criteria but they are more consistent with the calculated Poole-Frenkel conduction values. In addition, their estimated Schottky relative permittivities are shown to be equal to or less than unity, implying a transparent material, whereas the CuPc exhibited a strong bluish colour even when irradiated. Consequently the Poole-Frenkel bulk limited conduction mechanism is suggested to be appropriate.

γ-Ray Exposure Dose (Gy)	Relative Permittivity (ϵ_r)	Refractive Index (n_i)	Colour Centre Density (N_f) ($cm^{-1}x10^{20}$)
As-depos.	4.4	2.10	2.06
180	5.0	2.24	4.51
360	5.7	2.39	6.50
540	6.4	2.53	8.30
720	7.4	2.72	11.05
900	8.9	2.98	14.72
1080	4.8	2.19	3.41

Table 2. *The relative permittivity and colour centre density show significant changes as the samples irradiated. The values of ϵ_r and N_f for the irradiated CuPc samples were higher than those for the as-deposited.*

The change in the conduction mechanism of CuPc thin films from a space-charge-limited conduction mechanism to a Poole-Frenkel may be attributed to the increase in carrier concentration caused by γ-radiation exposure. That is, as the carrier concentration within the CuPc thin film increases, the bulk resistance decreases and becomes comparable to the metal-insulator interface resistance leading to a bulk-limited conduction. Hence, the current will cease to rise rapidly for V > 1.8 V [18]. This is clearly illustrated by I-V characteristics in Figure 3 where the apparent space-charge-limited conduction with an exponent of 3.5 for the as-deposited films is converted to a Poole-Frenkel having an exponent of less than quadratic for the irradiated films.

4. Radiation Dosimetry using CuPc

Both of the B and Q absorbance bands experienced large rises when the CuPc thin films were exposed to γ-rays. Figure 5 shows a clear linear relationship between the absorbance and the absorbed radiation dose at the centre of the Q-band (615 nm). A maximum γ- radiation dose of 0.9 kGy is displayed by the linear dependence for the as-deposited CuPc samples. This linear relationship between the absorbance intensity at 615 nm and the radiation doses validated the use of copper phthalocyanine as an optical sensor dosimeter for γ-radiation. The initial optical conditions were restored by annealing the CuPc thin films for one hour at 323 K as illustrated by the plot of the annealed sample in Figure 1b. The same linear behaviour as that of the as-deposited was observed for the annealed, but at a lower absorbance, indicating a better amorphous structure and more radiation hardness. The annealed samples showed a maximum γ-radiation dose of 1.3 kGy (Figure 5).

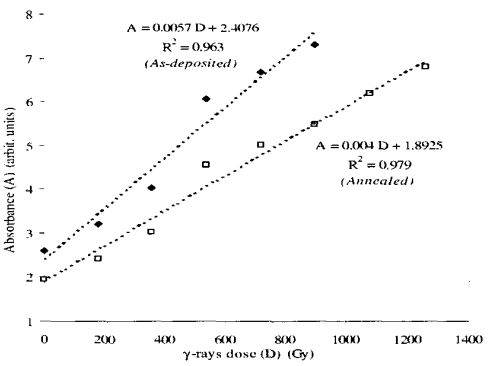

Figure 5. *Linear dependence of absorbance at the centre of the Q-band (615 nm) on γ-ray doses: The annealed sample displayed a higher radiation tolerance than the as-deposited sample.*

The maximum doses of 0.9 kGy and 1.3 kGy for the as-deposited and annealed films can be expanded by using smaller geometry. The absorbances at the centre of the Q-band (615 nm) for the as-deposited and annealed films are 2.6 and 1.95 respectively (see Figure 1). The lower absorbance of the annealed CuPc films is believed to result from the better-ordered amorphous structure. Annealing is known to be associated with the void removal and the atomic rearrangement of the amorphous structure in thin films [19]. Annealing is also known to play an important role in changing the internal bulk structure of the amorphous thin film layers and decrease the structural disorders [20].

5. Summary

Copper phthalocyanine thin films prepared by thermal vacuum deposition displayed high sensitivity to γ-rays. When the samples were annealed for one hour at a temperature as low as 323 K, they showed higher radiation tolerance. The low annealing temperature and the flexibility of saturation level are of high preference in designing optical sensor dosimeters, which can incorporate the absorbance, the density of colour centres or the refractive index as a tool of measurement. The effects of γ-radiation on the

absorbance bands, permittivity and conduction mechanisms of thermal vacuum deposited copper phthalocyanine thin films were investigated. Linear relationships were observed for the effect of γ-radiation on absorption bands. The conduction mechanism is believed to change from the space-charge-limited mechanism for the as-deposited to Poole-Frenkel when irradiated. The relative permittivity values of the as-deposited CuPc films were shown to be within the range of the discrepancy reported by other workers. The irradiated Al/CuPc/Al devices, on the other hand, displayed large increase in permittivity from the as-deposited for different radiation doses. It is proposed that the linear behaviour of the radiation-induced variations in absorbance or permittivity of copper phthalocyanine thin films can be a useful indicator for radiation dose measurements and optical sensor dosimeters. The CuPc thin films are chemical and heat stable and they are easily fabricated by subliming the material at a relatively low temperature (823 K). The thermally deposited CuPc films are of high purity [5, 7, 16]. Consequently, the thermally deposited copper phthalocyanine thin films are recommended as an optical sensor dosimeter.

6. References

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