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Electrical properties of chloroaluminium phthalocyanine thin film sandwich devices

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Spectroscopic measurements in the range 10 kHz - 6 MHz at different temperatures are reported for Au/ClAlPc/Au thin film sandwich devices. The *ac* conductivity was found to vary with the angular frequency ω. In the high frequency region, the *ac* conductivity is proportional to ω^n. The capacitance and loss tangent decrease with increasing frequency and the capacitance increases with increasing temperature. The results show that the relative importance of the hopping model and band theory in describing the film conduction with regard to the operating conditions. The band theory is dominant at high temperatures and low frequencies, whereas hopping model is dominant at high frequencies and low temperatures.

Keywords: Electrical properties, Chloroaluminium phthalocyanine,Thin film, Sandwich devices

IPC Code: G01R

1 Introduction

Recently, with the increase levels of atmospheric pollutants, various metal phthalocyanines (MPc's) are under intensive investigation. To ascertain their suitability as viable gas sensing materials. The performance of phthalocyanines as gas sensors is based on large changes (several orders of magnitude) in the dark conductivity which is directly related to the adsorption ppm or even ppb levels of toxic gases such as NO_2, NH_3, Cl_2, etc. on the surface of metal phthalocyanine (MPc) films[1-4]. It is also known that structure and morphology of phthalocyanine thin films can strongly influence their gas-sensing characteristics[5,6]. The behaviour of these materials is normally studied by two main ways, optically (usually optical absorption measurements) and electrically (using planar or sandwich devices).

The planar devices consisting of thin films with interdigital gold (Au) electrodes are primarily used as gas sensors and also to observe the materials response to various gases by *dc* electrical characteristics, whereas sandwich devices can be used for *ac* measurement of capacitance as well. The *dc* electrical properties of phthalocyanine thin films devices have been extensively studied in recent years[7,8]. There is no more information in the literature on chloroaluminium phthalocyanine (ClAlPc) which we expect to be a more sensitive and more stable material for gas sensor fabrication based on previous optical measurements and thermo gravimetric results on chloroaluminium phthalocyanine[9]. In the present investigation, *ac* electrical measurements were carried out as a function of temperature to study the electronic structure of ClAlPc thin films and identify the conduction mechanism operating under different conditions.

2 Experimental Details

Au/ClAlPc/Au thin film sandwich devices were prepared by sequential thermal evaporation under a vacuum of approximately 10^{-5} mbar onto pre-cleaned glass substrates. The substrates were kept at room temperature during evaporation. The ClAlPc material was prepared in-house from 20 g of phthalonitrile, 5 g of $AlCl_3$ which was refluxed in 100 ml of quinoline at 400 K for 2 h. The product was filtered and the resulting precipitate was washed sequentially in toluene, carbon tetrachloride and acetone. The product was then dried at 390 K ready for evaporation. The ClAlPc evaporation rate used was 0.2 nm per second and the thickness was monitored during deposition using a quartz crystal monitor. All the measurements reported in this investigation were performed on films of thickness 3 μm. The evaporation rate of gold was 0.1 nm per second and the thickness of the resulting Au films was 100 nm. A specially designed stainless steel chamber was used to enable electrical measurements to be made over a wide temperature range. The devices were attached in good thermal contact to a substrate holder which could be heated using a thermofoil heater (Minco HK-913). Sample temperatures were monitored to an accuracy of 1 K with a chromel-alumel thermocouple. All devices used in the present investigation were annealed overnight in a vacuum of 10^{-5} mbar at 400 K prior to the measurements.

The following electrical measurements were then made with the film in the dark via screened leads from the vacuum chamber to a Hewlett-Packard 4275A LCR multi-frequency meter.

(i) *ac* dependence of capacitance on frequency and temperature in the range 10^4- 6×10^6 Hz and 290 - 390 K, respectively.

(ii) *ac* dependence of loss tangent (tanδ) for the same range of frequency and temperature in the range 290-420 K. From these data, conductivity versus frequency, and activation energy graphs (σ against 1/*T*) were also plotted.

3 Results

3.1 Capacitance and Loss Tangent

The capacitance of chloroaluminium phthalocyanine (ClAlPc) thin film sandwich devices as a function of frequency in the frequency range 10^4-6×10^6 Hz were measured at 300, 340, 365 and 390 K for a film thickness of 3 µm as shown in Fig. 1. The capacitance was found to be strongly frequency dependent at relatively high temperatures and low frequencies. The change in capacitance with frequency is less at low temperatures and high frequencies. The capacitance in copper, lead and molybdenum phthalocyanine films shows a similar decrease with increasing frequency[7]. These results are more clearly shown in Fig. 2, where the capacitance is plotted as a function of temperature for the frequencies of 10^4-6×10^6 Hz. The capacitance is strongly frequency dependent at high temperatures (Fig. 2). Both results shown in Figs 1 and 2 can be described by the theory of Goswami *et al.*[10] for ZnS films. In this proposed model, each capacitor system is assumed to comprise an inferred capacity element *(C)*, which is unaffected by frequency and temperature, and a discrete resistance element *R* due to the dielectric film in parallel with *C*. Both *R* and *C* are in series with resistance *r* due to lead length, etc. Such a model seems to be more appropriate in the present work, as gold electrodes are known to provide ohmic contacts with phthalocyanines[11] but blocking contacts are provided by aluminum electrodes[12]. In the present case, there is also a decrease in loss tangent (tanδ) with increasing frequency as shown in Fig. 3. The tanδ versus frequency characteristics at different temperatures display a loss tangent

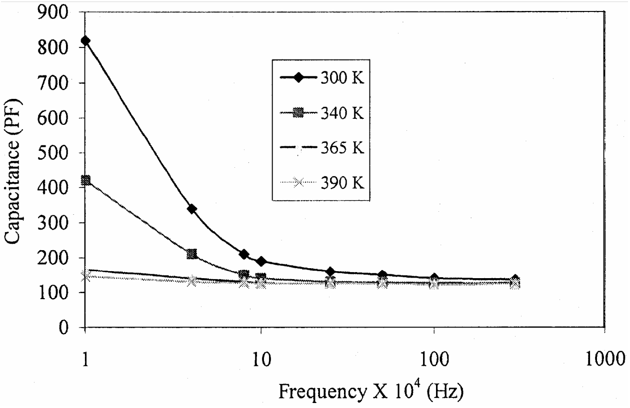

Fig. 1—Variation of capacitance with frequency at different temperatures

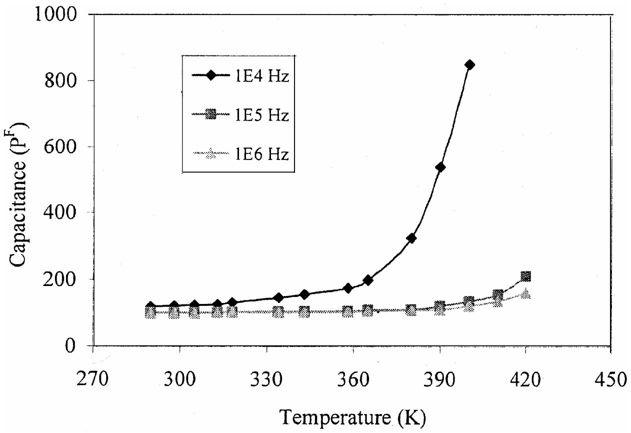

Fig. 2—Variation capacitance with temperature at different frequencies

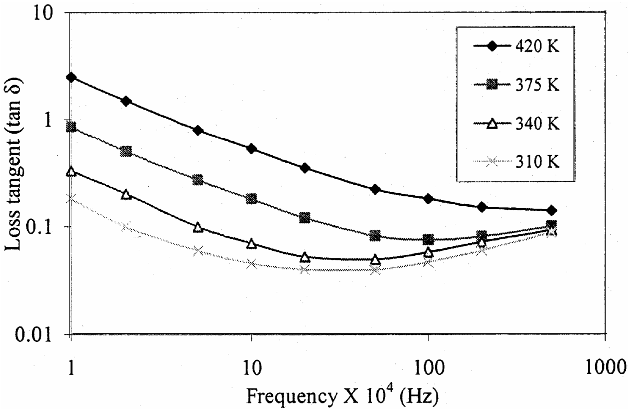

Fig. 3—Variation of tan δ with frequency at different temperatures

minimum ($\tan\delta_{\min}$) which shift to higher frequency with increasing temperature. The shift of $\tan\delta_{\min}$ towards lower frequencies with increasing temperature should be related to the decrease of R with increasing temperature. The value of $\tan\delta_{\min}$ also increases with increasing temperature. According to Goswami model the capacitance (C_s), the loss tangent ($\tan\delta$) and the equivalent series resistance (R_s) are given by:

$$C_s = \frac{1+\omega^2R^2C^2}{\omega^2R^2C} = C + \frac{1}{\omega^2R^2C} \qquad \ldots (1)$$

$$\tan\delta = \frac{1}{\omega RC}\left(1+\frac{r}{R}\right) + \omega r C \qquad \ldots (2)$$

$$R_s = r + \frac{R}{\omega^2R^2C^2+1} \qquad \ldots (3)$$

respectively, where ω is the angular frequency.

Eq. (1) predicts that with increasing frequency the measured capacitance (C_s) should decrease and at high frequency C_s should fall to the constant value of C; also for any frequency C_s will increase with increasing temperature because of the decreasing value of R ($R=R_0\exp\Delta E/kT$). as shown in Figs 1 and 2. For Au/ClAlPc/Au thin film devices, we have $R>>r$ hence the loss tangent ($\tan\delta$) can be written as $\tan\delta = 1/\omega RC + \omega rC$. In this equation, the expression for the loss tangent predicts that at high frequency the ω term is dominant while at low frequency the term in 1/ω dominates. So Eq. (2) predicts a decrease in tanδ with increasing frequency at low frequency followed by a loss tangent minimum ($\tan\delta_{\min}$) at $\omega_{\min} = [1/rRC^2]^{1/2}$ and an increase in loss tangent with increasing frequency at high frequency.

3.2 Conductivity

The conductivity may be defined using the relation:

$$\sigma(\omega) = \sigma_0(\omega)\, e^{\frac{-Et}{kT}} \qquad \ldots (4)$$

where Et is the activation energy, k is Boltzmann's constant and σ_0 represents the value of σ at $1/T = 0$. The variation of conductivity (σ) as a function of $1/T$ at constant frequencies (10 kHz, 100 kHz and 1 MHz) is shown in Fig. 4. It is found that the value of σ is strongly dependent on frequency with considerably higher values at higher frequencies. The *ac* conductivity data of our Au/ClAlPc/Au thin film devices were plotted as a function of frequency at constant temperature as shown in Fig.5. In the temperature range ≥323 K and at low frequencies in each case a distinctive linear region was observed in the conductivity-frequency (σ-*f*) characteristics of these devices. At low frequencies, the slopes of lnσ versus ln*f* plots are approximately equal to 0.1. Beyond the low frequency region, the slope increases with increasing frequency to reach a constant value of 1 ± 0.1 which is constant over the high frequency region. The high and low frequency regions are clearly identified in Fig. 5. The increase of the slope with increasing frequency may be connected with the onset of hopping conduction which shifts towards the higher frequencies with increasing temperature. The onset frequency of hopping conduction at different temperatures in each case is indicated by the knee in the curve of Fig. 5. The conductivity at low frequency

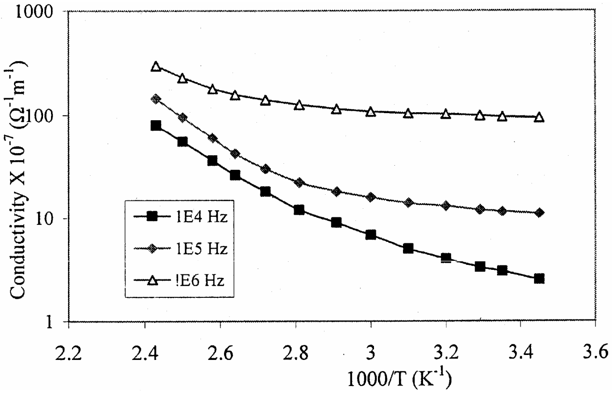

Fig. 4—Dependence of *ac* conductivity on (1/*T*) at different frequencies

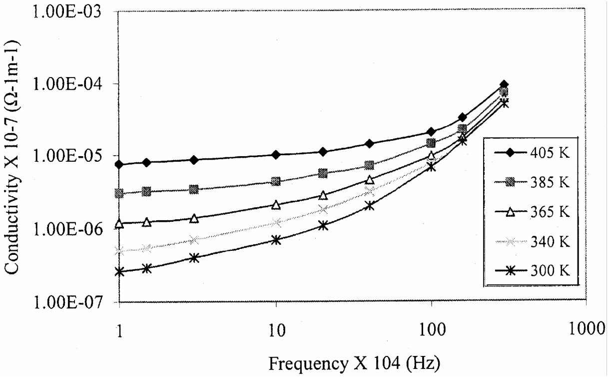

Fig. 5—Dependence of *ac* conductivity on frequency at different temperatures

increases only slightly with increasing frequency and may be regarded as constant with ω. The low frequency conductivity could, therefore, be dominated by electronic transitions between the valence band and trap levels can be adequately interpreted by the band model. Our results give further evidence for the importance of hopping mechanism at low temperature and at high frequencies while the conduction mechanism is mainly of the band type in the high temperature and low frequency region.

4 Conclusions

Au/ClAlPc/Au thin film devices were fabricated for *ac* conductivity measurements in the frequency range 10 kHz-4 MHz at different temperatures. The capacitance of devices prepared by thermal evaporation was found to be sensitive to frequency variation especially at higher temperatures. The capacitance has been observed to decrease with increasing frequency and also to increase with increasing temperature. The mechanism which controls the conductivity of Au/BrAlPc/Au devices depends on the device temperature and applied frequency. The results show that both the hopping and band-type mechanisms may be functioning, but, depending on the conditions of experiment, one of the two mechanisms predominants. It is found that the conduction mechanism is mainly hopping at low temperatures and high frequencies and it is band-type at high temperatures and low frequencies.

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