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DIELECTRIC AND AC CONDUCTION STUDIES OF LEAD PHTHALOCYANINE THIN FILM

P. KALUGASALAM[a*], DR.S. GANESAN[b]
[a]*Department of Physics, Tamil Nadu College of Engineering, Coimbatore*
[b]*Department of Physics, Government College of Technology, Coimbatore*

The thin film of Lead Phthalocyanine (PbPc) on glass was prepared by Vacuum deposition method. Deposition of PbPc on pre-cleaned glass substrates under the pressure of 10^{-6} Torr was achieved by slowly varying the current. The rate of evaporation was properly controlled and maintained constant during all the evaporations. The thicknesses of the films were 150 nm, 300 nm and 450 nm. Dielectric and conduction properties of Lead Phthalocyanine thin films have been studied. The capacitors were formed on a substrate with the dielectric layer in between the two metal electrodes so as to form an MSM structure. The variation of capacitance with frequency at different temperatures of PbPc films for thickness 450 nm was observed. This dependence of conductivity on frequency can be explained by the predominance of the hopping mechanism, as the conductivity increases with increasing frequency

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1. Introduction

Metal phthalocyanines (MPc's) have received increasing attention over the last decade due to their potential applications in gas sensing devices [1]. They are organic semiconductors exhibiting high chemical and thermal stability. Semiconducting behaviour of phthalocyanine thin films is p-type at all temperature [2].

Dielectrics are basically insulator materials having a special property of storing and dissipating electrical energy when subjected to electromagnetic fields. Some semiconductors have also similar properties. Studies of these materials particularly in ac fields provide an insight of the electrical nature of the molecular or atomic species which constitute the dielectric materials [3]. An important aspect for the study of the dielectric properties of materials is to understand certain physical properties of the system, like the presence of impurities, voids, structural defects, various polarization and relaxation mechanics etc. [4].

The electrical and gas sensing properties of phthalocyanines are critically dependent on a range of material parameters, including film morphology, which in turn is determined by the preparation parameters such as deposition rate, substrate temperature and post deposition annealing[2, 5, 6]. AC measurements yield information which can be used to determine whether the intrinsic conduction process within the film itself can be described by the hopping model or band theory, under particular operating conditions [7]. In short both dielectric and ac conductivity phenomena yields information about the mechanism of conduction in thin films.

The present work is a detailed study on dielectric properties of Al-PbPc-Al structures and ac conduction studies of PbPc films of thickness 450 nm deposited on glass substrates.

[*] Corresponding author: Kaluguindian@yahoo.co.in

2. Experiment

The powder of lead phthalocyanine (80% dye, sigma Aldrich company, Bangalore, India) was kept in a molybdenum boat of 100 amps and heated with high current controlled by a transformer. The transformer is capable of supplying 150amps at 20volts is used to provide the accessory current for heating the molybdenum source which was used for the evaporation process. Prior to each evaporation, the evaporant material was carefully degassed at lower temperature for about 45 minutes with the shutter closed. Deposition of PbPc on pre-cleaned glass substrates under the pressure of 10^{-6} Torr was achieved by slowly varying the current. The rate of evaporation was properly controlled and maintained constant during all the evaporations. Rotary drive was employed to maintain uniformity in film thickness. The thickness of the films was measured by Quartz crystal monitor. The adhesion of the films to the substrate seems to be extremely good. The samples prepared in a similar environment were used for studying their various properties.

3. Fabrication of thin film capacitors

The capacitors were formed on a substrate with the dielectric layer in between the two metal electrodes so as to form an MSM structure.

3.1 Selection of electrode material

Electrode should adhere well to the substrate to form a stable structure. The electrode material should be such that it should not react with the material of the electric film and should have a low electrical resistance. Generally metals like gold, silver, copper, aluminium, titanium, lead and tin have been used as electrode materials. Of this gold, silver and copper have very low resistance but their adherence to the substrate is poor. Titanium, lead and tin have good adhesion but offer high resistance. Only aluminium has been established to possess both qualities and has been used for electrode deposition in the present work.

3.2 Electrode deposition

Aluminium (99.999% purity, Aldrich chemicals, USA) was evaporated at a pressure of 10^{-6} Torr from a helical tungsten filament through masks to form the lower electrode. Aluminium melts, wets the filament and results in uniform coating. The source to the substrate distance was maintained as 13.5 cm prior to the evaporation; aluminium was kept under shutter for two minutes. The required dielectric films have then been coated with the aid of suitable brass masks. Finally the upper electrode was formed with aluminium to complete MSM structure. The electrode shapes and the final MSM structure are shown in Figure 1.

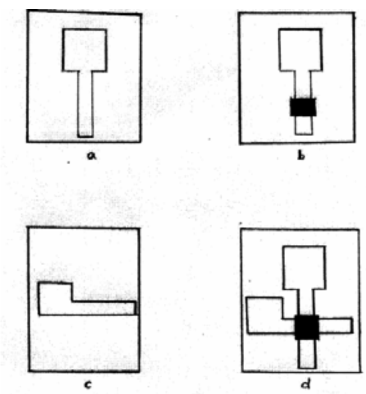


Fig. 1. Formation of (a) top electrode (Al) (b) dielectric layer (PbPc) over the top electrode (c) bottom electrode and (d) the final MSM structure.

4. Measurements

The capacitance and loss factor are the two vital parameters in the dielectric studies. The dielectric studies on PbPc films were carried by forming Metal-Semiconductor-Metal (MSM) structures. PbPc was deposited over aluminium electrodes coated on glass substrate. This acts as bottom electrode of the capacitor and aluminium coated on the surface PbPc acts as top electrode, to form a capacitor. The capacitance (C) and the dissipation factor (D) for MSM structure in the frequency range 20 Hz to 100 kHz at different temperatures (300 to 483 K) were measured using a Digital LCR meter (LCR-819, GW Instek, Goodwill Instrument Company Ltd., Taiwan). Area of the capacitor was measured using traveling microscope. All the measurements were carried out under a rotary vacuum condition. A copper-constantan thermocouple is employed to sense the temperature.

5. Results and discussion

5.1. Effect of frequency and temperature on capacitance

Figure 2 shows the variation of capacitance with frequency at different temperatures of PbPc films for thickness 450 nm. The capacitance decreases with increasing frequency for all temperatures and attain a constant value at higher frequency. The capacitance is shown to be strongly frequency dependent at relatively high temperatures and at low frequencies, but became less at low temperatures and at high frequencies. This result is associated with the slow release of charge carriers from relatively deep traps [13,14].

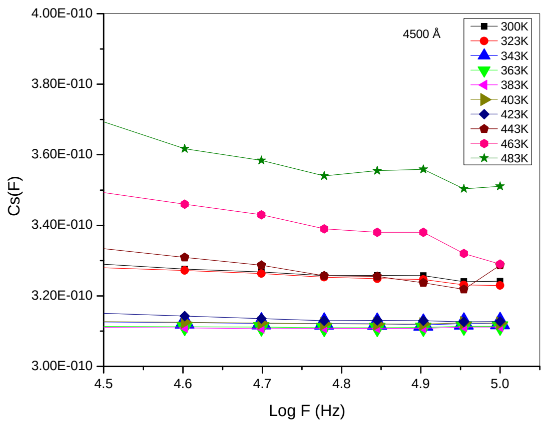


Fig. 2. Variation of capacitance with frequency at different temperatures.

The change of capacitance with frequency reduces as the temperature decreases. At higher temperatures, the variation of capacitance with frequency may be attributed to the blocking of charge carriers at the electrodes. Actually the charge carriers present in the film migrate upon the application of the field and because of the impedance to their motion at electrodes there is a large increase in the capacitance at low frequencies. Similar behaviour has been reported by researchers on semiconducting films [15].

The variation of dielectric constant with frequency of PbPc thin films is shown in Figure 3. From the graph it is clear that dielectric constant decreases with increasing frequency. The decrease in ε’ may be due to the decrease in space charge carries or interfacial polarization in the films [16, 17]. It is also observed that the dielectric constant increases with increase in temperatures at all frequencies and this parameter is related to the conductivity of the films because the conductivity increases as the temperature increases. The increase of the dielectric constant with decrease in frequency can be attributed to the presence of dipoles [15].

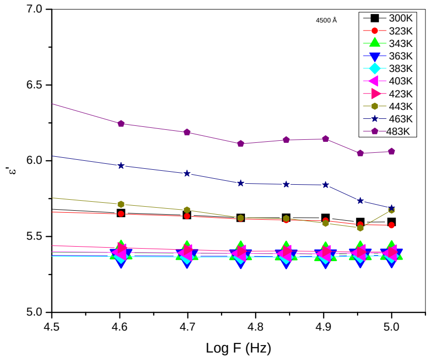


Fig. 3. Variation of dielectric constant with frequency at different temperatures.

The variation of tanδ with logarithmic frequency is shown in Figure 4. From the graphs it is observed that tangent factor increases with increase in frequency and is almost constant at low frequencies for lower temperatures. It may be due to the effect of lead resistances [18].

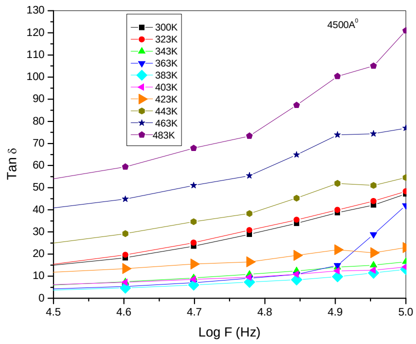


Fig. 4. Variation of tan δ with frequency at different temperatures

5.2. Temperature coefficient of capacitance and permittivity

Figure 5 illustrates the variation of capacitance with temperature of PbPc thin films. From the graphs it is observed that capacitance increases with temperature at all frequencies. This effect is interpreted as arising from an increase in the number of free carriers with increasing temperature [14, 18]. The TCC value for PbPc films of thickness 450 nm at 50 kHz is 0.203 x 10^{-3} ppm / K.

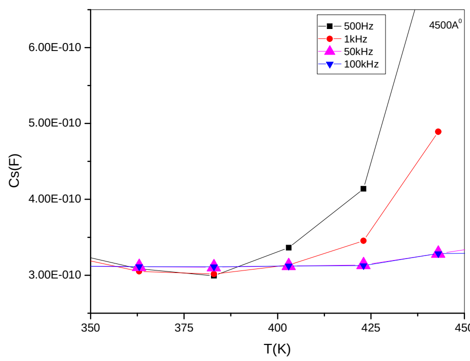


Fig. 5. Variation of capacitance with temperature at different frequencies

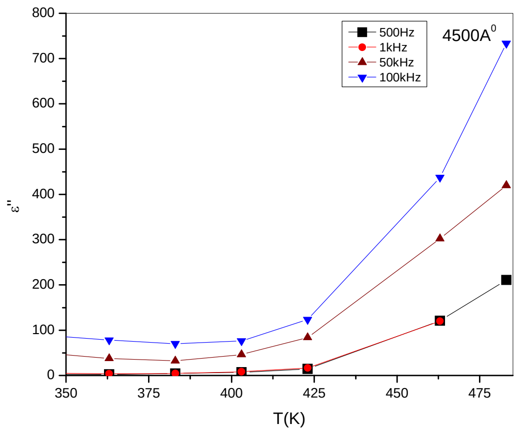


Fig. 6. Variation of dielectric permittivity with temperature at different frequencies.

The variation of permittivity with temperature of PbPc thin films is shown in Figure 6. It is clear that permittivity increases with increase in temperature. The TCP value for the above said film at 50 kHz is 0.098 x 10^{-3} ppm / K.

5.3. AC conduction

Figure 7 shows the variation of ac conductance with frequency at different temperatures. It is clear that conductivity is strongly frequency dependent. The conductivity increases with increasing frequency according to the relation

$$\sigma(\omega) \alpha \omega^n$$

where ω is the angular frequency and the value of n depends on the temperature and frequency. The value of n is found to be in between 0.8 and 1. This dependence of conductivity on frequency can be explained by the predominance of the hopping mechanism, as the conductivity increases with increasing frequency [14].

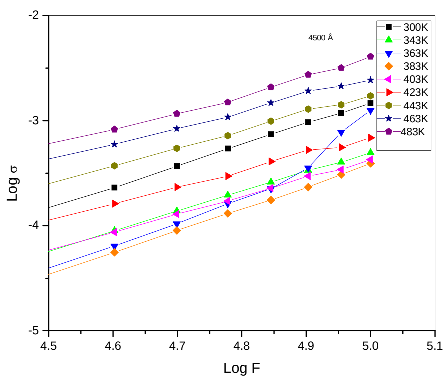
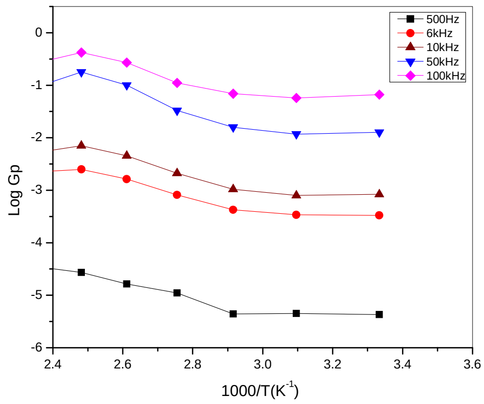
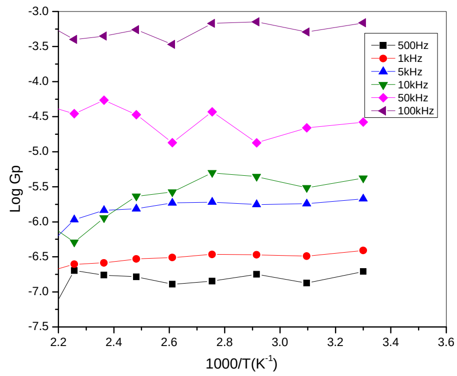


Fig. 7. Variation of ac conductance with frequency at different temperatures.

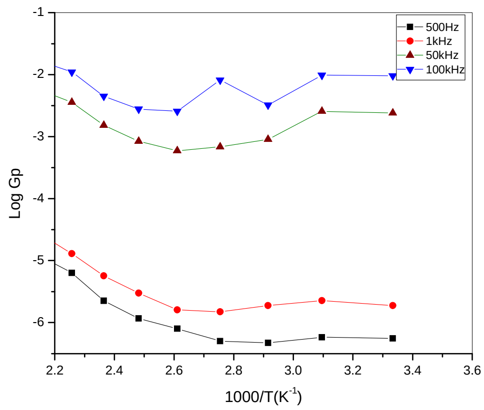
Variation of log Gp vs inverse temperature of PbPc films for thickness a) 150 nm, b) 300 nm, c) 450 nm are shown in Figure 8. In all cases conductivity is strongly temperature dependent although the frequency dependence is less pronounced at higher temperatures. In the higher temperature range the conductivity remained essentially constant over the whole frequency range.



(a)



(b)



(c)

Fig. 8. Variation of log Gp vs inverse temperature of PbPc films for thicknesses
a) 150 nm b) 300 nm c) 450 nm

The activation energies have been determined from the slope of 1000/T vs log Gp curves at different frequencies and it is illustrated in Table 1. It is observed that activation energies increase with increase in thickness and decreases with increase in frequencies. This may be due to the increase of the applied field frequency which enhances the electronic jumps between the localized states [19].

The dependence of conductivity on inverse temperature showed a region of free-band conductivity with activation energy of about 0.3 eV at higher temperatures and lower frequencies and very low activation energies associated with hopping at lower temperatures and higher frequencies [13].

Table 1. Activation energies of PbPc films for different thicknesses at different frequencies.

Frequency / Thickness	Activation energy (eV)		
	150 nm	300 nm	450 nm
500 Hz	0.3584	0.3772	0.4243
50 KHz	0.2688	0.2828	0.3639
100 KHz	0.1219	0.1591	0.2427

AC measurements have generally shown a $\sigma \propto \omega^n$ dependence for low temperatures and high frequencies, corresponding to hopping conduction. At higher temperatures and low frequency free-band conductivity is observed. Capacitance and loss tangent variations with both frequency and temperature have been accounted for using various equivalent circuit models applicable to ohmic and blocking electrodes [13].

6. Conclusion

The capacitance decreases with increasing frequency for all temperatures and attain a constant value at higher frequency. The charge carriers present in the film migrate upon the application of the field and because of the impedance to their motion at electrodes there is a large increase in the capacitance at low frequencies. The dielectric constant decreases with increasing frequency. The decrease in dielectric constant is due to the decrease in space charge carries or interfacial polarization in the films. The dielectric constant increases with increase in temperatures at all frequencies and this parameter is related to the conductivity of the films because the conductivity increases as the temperature increases. The increase of the dielectric constant with decrease in frequency can be attributed to the presence of dipoles.

The conductivity is strongly frequency dependent. The conductivity increases with increasing frequency. This dependence of conductivity on frequency can be explained by the predominance of the hopping mechanism, as the conductivity increases with increasing frequency. The activation energies increase with increase in thickness and decreases with increase in frequencies. It's due to the increase of the applied field frequency which enhances the electronic jumps between the localized states.

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