

Comparison Studies of Dielectric and AC Conduction of PbPc and CuPc Thin Films

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Abstract - The thin film of Lead Phthalocyanine (PbPc) and Copper Phthalocyanine (CuPc) on glass are prepared by Vacuum deposition method. Deposition of PbPc and CuPc on pre-cleaned glass substrates under the pressure of 10^{-6} Torr are achieved by slowly varying current of 20 Volt. The rate of evaporation is properly controlled and maintained constant during all the evaporations. The thicknesses of the films are 150 nm, 300 nm and 450 nm on glass substrate. Dielectric and AC conduction studies of Lead Phthalocyanine and Copper Phthalocyanine thin films have been studied. The variations of capacitance with frequency at different, permittivity with temperature, capacitance with temperature and ac conductance with frequency at different temperatures of PbPc and CuPc have been studied. The activation energies have been determined from the slope of $1000/T$ vs. $\log G_p$ curves at different frequencies (where $G_p = -E_g/RT$).

Keywords - Phthalocyanine, Dielectric, Permittivity, Activation energy, MSM structure.

I. INTRODUCTION

The search for materials suitable for low cost, versatile electronic devices has stimulated interest in organic thin film transistors [OTFTs] and sensors. It has led in recent years to an extensive investigation of a range of metal substituted phthalocyanines [1,2]. Application of OTFTs as chemical sensors has shown promise in the development of electronic noses and in nerve agent detection [3-5]. A key issue regarding the widespread production of OTFTs is the long term stability and device integrity in ambient operating conditions [6,7]. Among the small molecule based OTFTs, pentacene OTFTs have received significant attention regarding instability to ambient components such as oxygen and humidity [8-12]. Several mechanisms have been proposed to explain this instability in pentacene OTFTs, including water adsorption in grain boundaries [10,11] and oxygen generated impurities [13].

Phthalocyanines have potential applications in optical logic display devices, electrophotography, security printing, gas detectors [14], solar cells [15, 16], sensitizers and colour filters [17]. These materials are generally p-type semiconductors and have the advantage of being sufficiently stable towards chemicals and heat. They can be easily sublimed, resulting in high purity thin films without decomposition. The physicochemical properties can be altered by changing the metal ion. Film properties of this prototype organic semiconductor are dependent on the evaporation rate, substrate temperature and post-evaporation annealing [17, 18]. Photovoltaic devices made from organic pigments have reached power conversion

efficiency of a few percent [19, 20] that is much lower than those of their inorganic combinations.

In the present work, we have characterized lead phthalocyanine (PbPc) and Copper phthalocyanine (CuPc) in the form of Metal-Semiconductor-Metal (MSM) structures. We have studied dielectric, capacitance and AC conduction characteristics of Cupc and PbPc thin film sandwiched between Al and Al electrodes, with the aim to understand the increase of applied field frequency which enhances the electronic jumps between the localized states.

II. EXPERIMENTS

The powder of PbPc (80% dye, Sigma Aldrich company, Bangalore, India) is kept in a molybdenum boat (100 A current rating) heated with high current controlled by a transformer. The transformer is capable of supplying 150 amps at 20 volts which is used to provide the accessory current for heating the molybdenum source. It is used for the evaporation process. Prior to evaporation, the evaporant material is carefully degassed at lower temperature for about 45 minutes with the closed shutter. Thin films of PbPc are deposited at room temperature on pre-cleaned glass substrates under the pressure of 10^{-6} Torr using a (12 A 4D Hind Hivac, India) coating unit. The rate of evaporation is properly controlled and maintained constant during all the evaporations. Rotary drive is employed to maintain uniformity in film thickness. The thicknesses of the films are 150 nm, 300 nm and 450 nm. The thickness of the films is measured by Quartz crystal monitor. The current voltage studies on PbPc and CuPc films are carried by forming Metal-Semiconductor-Metal (MSM) structures. The electrode shapes and the final MSM structure are shown in Figure 1. The top electrode contact is made by evaporation of aluminum (Al) through an appropriate mask at a vacuum of 10^{-5} Torr. The resulting area of the device is about 1cm^2 . Electrical measurements are performed using a subsidiary vacuum system and maintained at a pressure of 1.3×10^{-3} Pa. This procedure is used for preparing PbPc and CuPc thin film on pre-cleaned glass substrate. For the current voltage (I-V) measurement, Keithley electrometer with built in power supply is used.

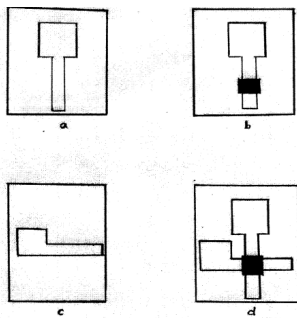


Fig.1. Formation of (a) top electrode (Al) (b) dielectric layer (PbPc) over the top electrode (c) bottom electrode and (d) the final MSM structure

III. 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 structures. PbPc is deposited over aluminium electrodes coated on glass substrate. This acts as bottom electrode of the capacitor and the aluminium coated on the surface MPC 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 is measured using travelling microscope. All the measurements were carried out under a rotary vacuum condition. A copper-constantan thermocouple is employed to sense the temperature.

The equivalent parallel capacitance (C_p) and series capacitance (C_s) are connected by relations.

$$C_p = C_s / (1+D^2) \text{ and } C_s = C_p (1+Q^2) / Q^2$$

where D is the dissipation factor and Q, the quality factor. The loss factor is given by,

$$\tan \delta = F \times D / 100$$

where D is the dissipation factor and F, the frequency.

The r.m.s. voltage applied across the thin film capacitor throughout the study was 1V. The dielectric constant was calculated from the measured values of capacitance (C), capacitor area (A) and dielectric film thickness (d) with the aid of the relation,

$$\epsilon' = Cd / \epsilon_0 A$$

IV. RESULTS AND DISCUSSION

4.1 Effect of Frequency and Temperature on Capacitance

The hot probe method is adopted to detect the type of majority carriers. The distribution of thermal vacancies in a small region of the film depends on the temperature at that region. In this method, charge carriers near the hot end have higher velocities than the cold end which produce an electric field. This field is positive if the carriers are electrons and negative if the carriers are holes.

PbPc and CuPc thin films are found to be p-type semiconductors from the hot probe measurements using band theory [18,21].

Figure 2 and 3 shows the variation of capacitance with frequency at different temperatures of PbPc and CuPc films respectively 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 temperature and low frequencies, but becomes less at low temperature and at high frequencies. This result is associated with the slow release of charge carriers from relatively deep traps [21,22].

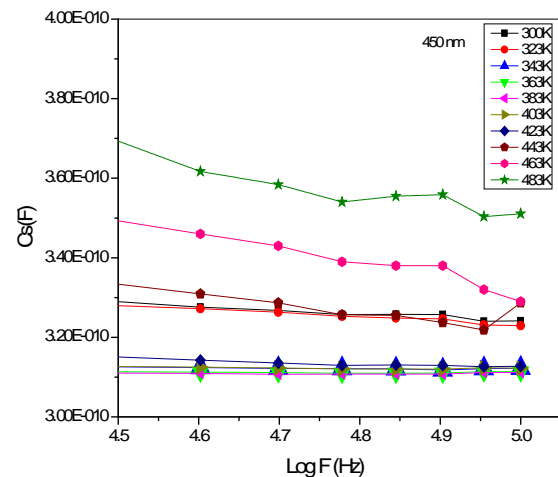


Fig.2. Variation of capacitance with frequency at different temperatures of PbPc

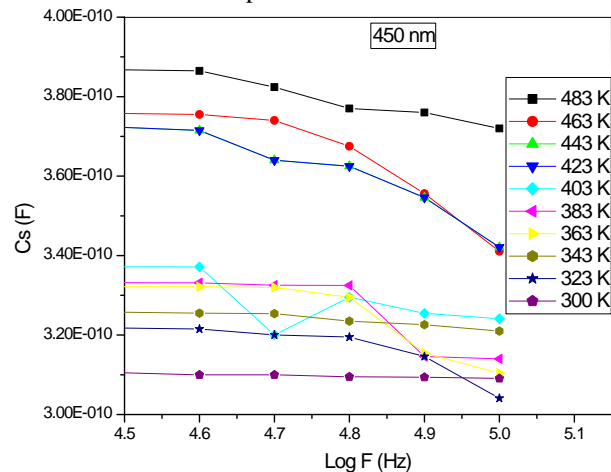


Fig.3. Variation of capacitance with frequency at different temperatures of CuPc

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. There is a large increase in the capacitance at low frequencies because of the impedance to their motion at electrodes. Similar behaviour has been reported by researchers on semiconducting films [23].

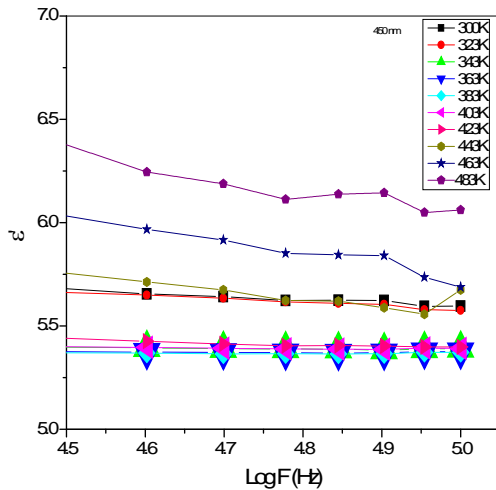


Fig.4. Variation of dielectric constant with frequency at different temperatures of PbPc

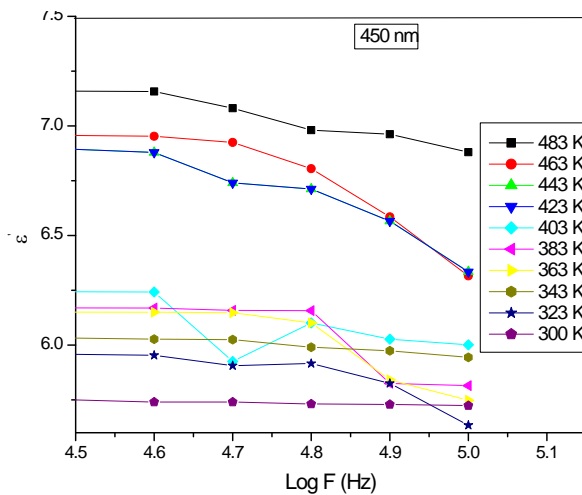


Fig.5. Variation of dielectric constant with frequency at different temperatures of PbPc

The variation of dielectric constant with frequency of PbPc thin and CuPc thin films are shown in figure 4 and 5 respectively. From the graphs, 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 [24]. It is also observed that the dielectric constant increases with increase in temperatures at all frequencies. 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 [23]. For CuPc, the dielectric constant should not increase with field. Figure shows the frequency dependence of the weak-field dielectric constant of the composite. The strong frequency dispersion is due to the space charge polarization (delocalized electrons) in CuPc, which will also result in frequency dependence of the strain response in the composite. The delocalized charge phenomenon in a composite in which insulation layers block the long-range space charge conduction to realize very high dielectric constant is analogous. In the ceramic capacitor where

semiconductor cores and insulation boundary-layers form the internal boundary layer capacitor, resulting in a material with dielectric constants exceeding 50,000 [25,26].

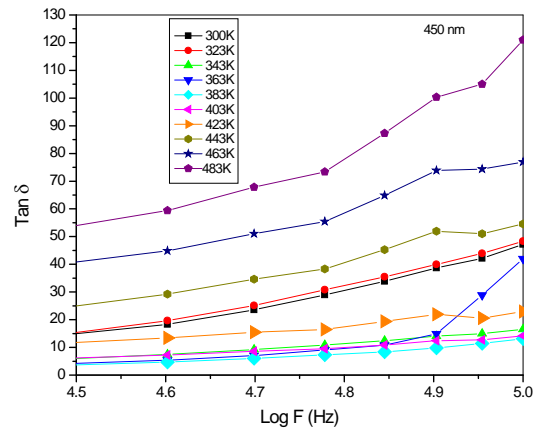


Fig.6. Variation of tan δ with frequency at different temperatures of PbPc

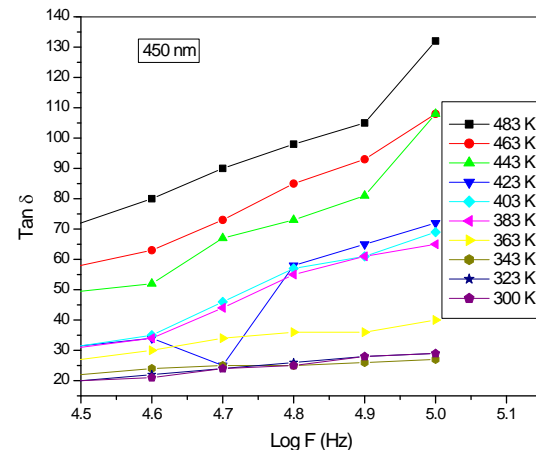


Fig.7. Variation of tan δ with frequency at different temperatures of CuPc

The variation of tan δ with logarithmic frequency of PbPc and CuPc are shown in Figure 6 and 7. 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 metal resistances [27].

4.2 AC Conduction

Figure 8 and 9 shows the variation of AC conductance with frequency at different temperatures of PbPc and CuPc thin films. It is clear that conductivity is strongly frequency dependent. The conductivity increases with increasing frequency according to the relation

$$\sigma(\omega) = \sigma_0 \omega^n$$
 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 from 0.8 to 1 for PbPc and 0.8 to 1.1 for CuPc. This dependence of conductivity on frequency can be explained by the predominance of the hopping mechanism, as the conductivity increases with increasing frequency [24].

The steady state transport properties in phthalocyanine are controlled by the presence and energy distribution of carrier sites. In the case of CuPc, the traps exist in thin films either as a single energy level or as a quasicontinuous energy distribution which is exponential in nature. It is suggested that the metal 3d orbitals provide an out-of-plane interaction with antibonding orbital's of nitrogen atoms in molecules situated in parallel planes above and below the structure [28]. Thus the central Cu metal atom adds another bridge for intermolecular charge transfer.

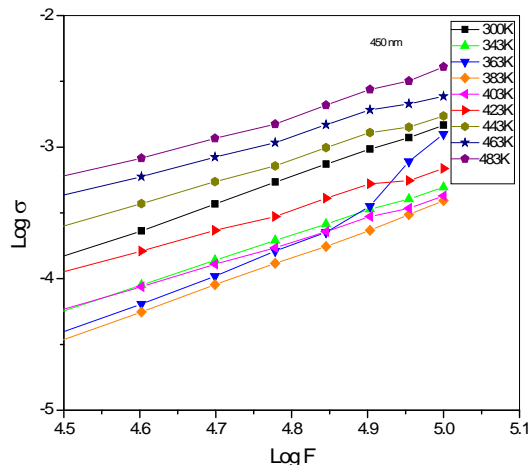


Fig.8. Variation of ac conductance with frequency at different temperatures of PbPc

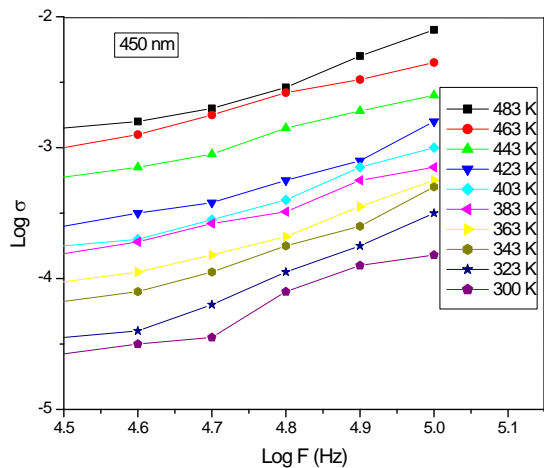
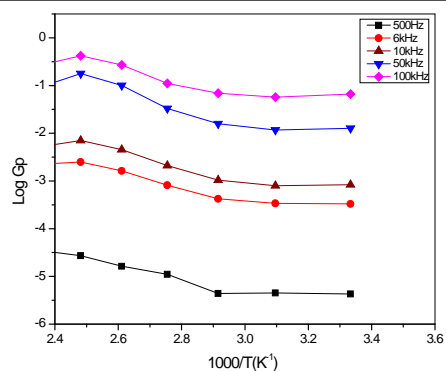
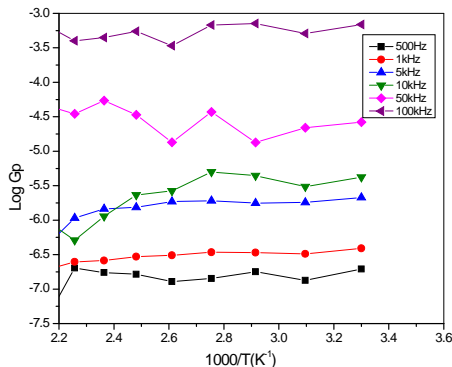


Fig.9. Variation of ac conductance with frequency at different temperatures of CuPc

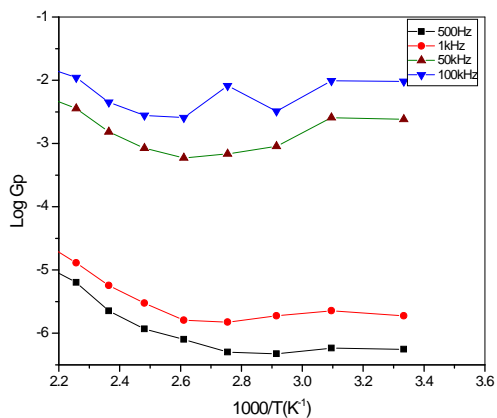
Variation of $\log G_p$ vs. inverse temperature of PbPc and CuPc films for thickness 150 nm, 300 nm and 450 nm are shown in Figure 10 and 11. In all cases conductivity is strongly temperature dependent although the frequency dependence is less pronounced at higher temperatures. In the higher temperature range, the conductivity remained essentially constant over the whole frequency range.



(a) 150 nm

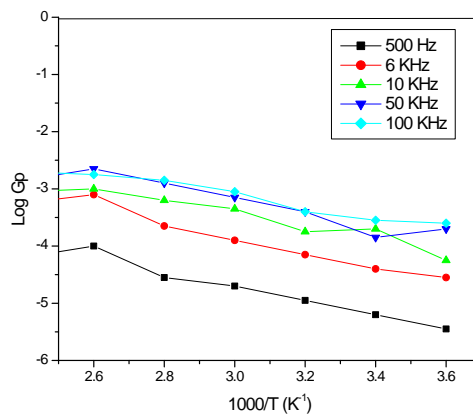


(b) 300 nm



(c) 450 nm

Fig.10. Variation of $\log G_p$ vs. inverse temperature of PbPc films for thicknesses



(a) 150 nm

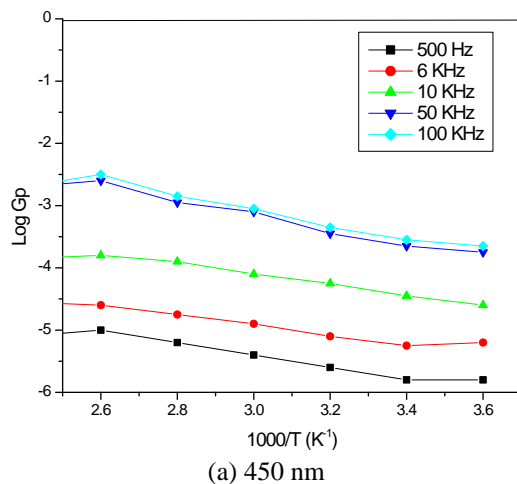
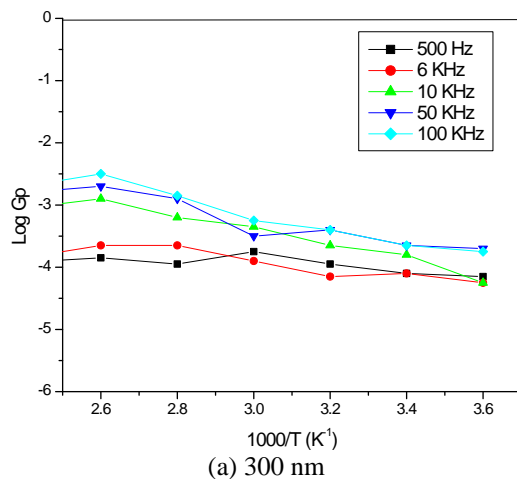


Fig.11. Variation of log Gp vs. inverse temperature of CuPc films for thicknesses

The activation energies have been determined from the slope of $1000/T$ vs. $\log G_p$ curves at different frequencies and it is illustrated in Table 1 and 2. It is observed that activation energies increase with increase in thickness and decrease 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 [29]. Activation energy of CuPc is higher than that of PbPc films. From the slope of the graph the activation energy is determined. The activation energy is determined within an accuracy of ± 0.01 eV in all the subsequent measurements. The activation energy of PbPc and CuPc are 0.4243 eV and 1.5073 eV for thickness 450 nm of frequency 500 Hz.

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

Table 2 Activation energies of CuPc films for different thicknesses at different frequencies

Frequency Thickness	Activation energy (eV)		
	150 nm	300 nm	450 nm
500 Hz	1.1841	1.2562	1.5073
50 KHz	1.0985	1.1832	1.3319
100 KHz	1.0119	1.0916	1.1322

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. Very low activation energies are associated with hopping at lower temperatures and higher frequencies [21].

AC measurements have generally shown as $\propto \omega^n$ 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 [21].

V. CONCLUSION

AC conduction measurement shows the semiconductor properties corresponding to the hopping conduction mechanism. 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 in both PbPc and CuPc films. 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 decrease with increase in frequencies. It's due to the increase of the applied field frequency which enhances the electronic jumps between the localized states. Activation energy of CuPc is higher than that of PbPc films. From the slope of the graph the activation energy is determined. The activation energy is determined within an accuracy of ± 0.01 eV in all the subsequent measurements. The activation energy of PbPc and CuPc are 0.4243 eV and 1.5073 eV for thickness 450 nm of frequency 500 Hz.

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