Comparison of the Electrical Properties of ClAlPc and CuPc thin film Planar Devices

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Abstract

In this research ChloroaIminium and Copper Phthalocyanine(ClAlPc and CuPc)were purified twice, using entrained sublimitation techniques. Ohmic contacts were made on the samples using the electrical properties of both (ClAlPc and CuPc) were studied over a range of temperatures. The activation energies of these materials were measured using both forward and reverse current-voltage characteristic and then they were carnpared. It was found that ClAlPc has a lower activation energy than CuPc. Further, I found that in ClAlPc, the activation energies evaluated using forward and reverse bias differ significantly at low temperatures while in CuPc this did not occur.

Introduiction

Recently, with the increase in environmental awareness and the increasing levels of atmospheric pollutants, various metal phthalocyanine (MPc's) as p-type organic semic-onductors are now under intensive investigation to ascertain their suitability as viable gas sensing materials. The perfonnance of phthalocyanine as gas sensors is based on large changes (several order of magnitude) in the dark conductivity which are directly related to the adsorption of ppm or even ppb levels of toxic gases such as NO_2, NH_3, Cl_2 etc., the surface of MPc films [1-4]. It is also known that the structure and morphology of phthalocyanine thin films can strongly influence their gas-sensing characteristics [5-6].

The research into the behavior of these materials is normally carried out in two main ways, optically (usually optical absorption measurements) and electrically (using planar or "sandwich" devices). Planar devices consisting of thin films with interdigital gold

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(Au) electrodes are primarily used as gas sensors, and d.c also uses them to observe the material's response to various gases. Electrical characteristic, whereas sandwich devices can be used for a.c. measurements of capacitance as well.

The d.c. electrical properties of various-phthalocyanine thin film devices have been extensively studied in recent years [7-8], but relatively little work has been done on their a.c. electrical behavior [9]. D.c. measurements of dark current provide information on conduction processes in the devices, which makes it possible to determined whether the process is electrode limited or bulk limited [10] and this is done by varying the type of electrode, the applied electric field strength or the operating temperature.

Displacement of charge in localized electronic states result from defects, impurities or internal micro-interfaces. Jonscher [11] proposes that such dependence is universal and applicable to a wide range of dielectric materials regardless of their chemical.

physical structure or the type of dominant charge carrier. Gould et.al. [12] have performed similar work on polycrystalline thin films of copper phthalocyanine, which showed behavior consistent with a hopping conduction mechanism, as did the room temperature measurements on molybdenum phthalocyanine by James et al. [13].

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Particular interest has been shown in PbPc films, primarily for NO_2 sensing. Bott and Jones [14] have described their use in a prototype multi-sensor system for monitoring toxic. gases. CuPc has similar properties to PbPc, but exhibits less sensitivity to NO_2[15]. In addition CuPc thin films have been used as a basis for NH_3 and CCl_4 sensors [16]. A number ofphthalocyanine (ZnPc, FePC, CoPc, etc.) also exhibit a variation in d.c.

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conductivity when they are exposed to oxidizing gases [17]. There is however relatively little information in the literature on 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 [18].

The present work is a continuation of previous studies in our laboratory. The aim of the present work was both to extend our knowledge of CuPc and ClAlPc devices and to investigate the feasibility of utilizing the electrical behavior of ClAlPc in a viable NO_2 gas sensor. In particular we studied the temperature dependence of the dark conductivity of ClAlPc and CuPc thin film devices, and we report and discuss the results obtained.

The I-V data is characterised by diffusion and generation-recombination currents. These characteristics are greatly affected by the impurities and defects that are inevitably present in the material [19]. A semi-logarithmic plot of current or conductivity against inverse temperature should yield the activation energy of a material from Arrhenius relationship $KT \times \text{Log } I = -E_a$; where K is the Boltzmann constant. This relationship means that an Arrhenius plot of log I versus 1000/T should comprise a good straight line of negative slope from which the activation energy is estimated by E_a =-1000 KB in electron volts. It is expected that the value of E_a will vary between the band gap energy E_g and half band gap for a pure material [20]. A lower value will result from the effect of deep level defects situated in the band gap, especially near the middle [21] to equally interact with either band.

Experimental Details

Both chloroalminium and copper phthalocyanine(ClAlPc and CuPc) were purified twice using entrainer sublimation techniques.

Eight finger interdigital gold electrodes with a 100-nm gap were then fabricated photolithographic ally on pre-cleaned polyborosilicate glass substrates. The purified ClAlPc and CuPc were thermally evaporated over the electrode arrays in vacuum at a pressure of 10^{-6} torr. In this way, ClAlPc and CuPc thin film scnsor dcvices were

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produced with various thickness in the range 400-500 nm on substrates held at room temperature. The deposition rate of the material was 0.1-0.2 nms^{-1} the thickness were monitored during deposition using a quartz crystal monitor. The samples were left in a desiccator for 10 weeks prior to the present measurements. All measurements were performed with the samples mounted in the dark and undcr pressurc of 10^{-6} torr in vacuum with an Oxford chamber-type cryostat with a facility to allow external leads. The sample temperature was controlled with an intelligent temperature controller (ITC4). The ITC4 has a heater and sensor, which are connected to the sample mounting such that its temperature can be raised and measured. To lower the temperature a siphon of liquid nitrogen was_passed through the outer walls of the sample mounting.To ensure a good thermal contact between the mounting and the sample a heat sink compound was used between the two. Since the sample was assumed isolated from the surrounding electronics, the temperature of the mounting was assumed to be equal to that of the sample. Current-voltage (I-V) measurements were carried out in the temperature range 300-380 K up to 100 volts in reverse bias and up to the current limit in forward bias. The data were acquired using a remotely controlled pA meter with a d.c voltage source. The sample temperature was maintained with the ITC4 which was also remotely controlled by a personal computer. In all experiments the current limit was set to 10 mA and long intergration times were chosen between voltage steps to allow setrling of the current after a voltage change. The temperature variation of the I-V characteristics was used to investigate the conduction mechanism in the samples. From these profiles, reverse or forward current values over a range of temperatures were extracted at a certain single low voltage(10V) and plotted as a function of inverse temperature to yield the activation energy of the material.

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Results and Discussion

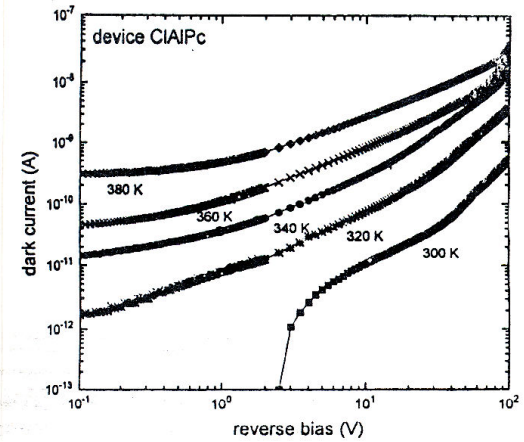


Fig. I: Temperature variatioll of the I-V characteristic in reverse bias for ClAlPc.

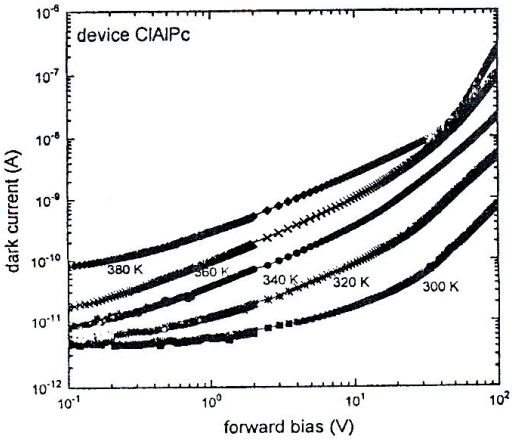


Fig. 2: The I-V characteristic as a function of temperature in forward bias for ClAlPc.

Figure 1 shows the reverse I-V characteristics for the ClAlPc device, and an immediate observation is the sudden and vertical increase of current with voltage of the 300 K curve.

This effect is explained later. Also, the current follows a $V^{1/2}$ variation at low voltages up to ? 2 volts. From 2 to 30 V the care ohmic. Beyond this voltage the curves show a space charge limited(SCL)behavior as the temperature sizes. At high temperature the current is saturated at low voltages. All these charestristics indicate that the device behaving like a semiconductor with defects as the temperature increases.

Figure 2 shows the forward I-V characteristics for the same ClAlPc device. Here, the reverse bias effect at 300K is not observed. The dark current is higher at high voltages. This occurs because of the ohmic behavior of the current over larger voltage ranges and also because of the SCL region is more defined. The ohmic behavior of the current is indicative of the presence of defect levels in the band gap[19] which act as recombination centers for any excess carriers, thereby reducing the carrier density and so increasing will show total ohmic behavior.

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The reverse and forward I-V characteristics for the CuPc device are shown in Figs. 3 and 4, respectively. The effect observed at 300K in the ClAlPc device is not seen for the CuPc device and this is explained later. The ohmic behavior of this device extends over a larger voltage range with the voltage at which the SCL effect occurs being more prominent. In reverse bias it occurs at ?75V while in forward bias it occurs at ? 20 volts. This means that-in reverse bias the defects near mid-gap allow more recombination and induce ohmic behavior. This effect is reduced in forward bias so that the SCL region shifts to lower voltages.

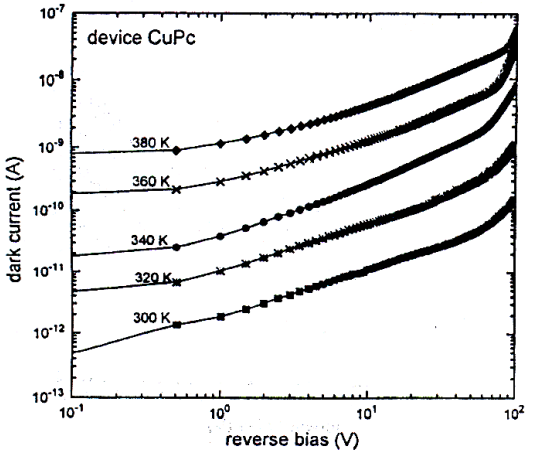


Fig. 3: Tile I-v characteristic as a function of temperature in reverse bias for a CuPc device.

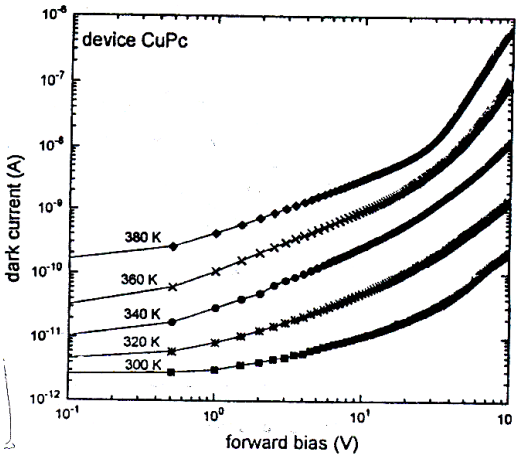


Fig. 4: A temperature variation of the 1-V Characteristic in forward bias for CuPc

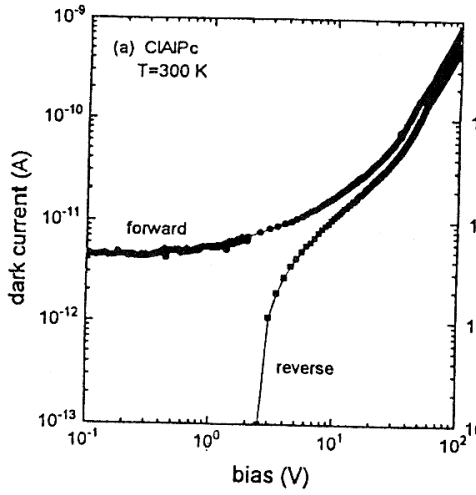


Fig. 5 (a): The I-V characteristic for ClAlPc, Device at 300 K (forward & revers)

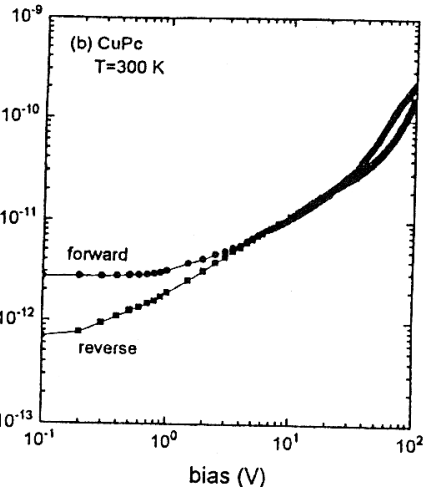


Fig. 5 (b): The I-V characteristic for CuPc Device at 300 K (forward & revers)

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Figure 5 shows the I-V characteristics for (a) ClAlPc and for (b) CuPc at 300K. At high bias voltages the curves are nearly similar with the current describing an ohmic behavior as outlined in the proceeding discussion. However, at low voltages the curves for reverse and forward bias deviate for CLALPc. This occurs because the structure of CLALPc molecule is not symmetrical, in that the Cl ion lies some distance from the central Al ion. This causes the molecule to be polarized under bias and to rotate, hence providing a different condition path for the current. This is confirn1ed by Fig.6(a) where it is shown that the activation energy is lower in the forward bias direction. In part (b) of Fig.5 there is very negligible deviation between the forward and reverse bias data and this is due to the CuPc structure being a symmetrical molecule and hence only impurities or defects would allow any polarization of the molecule to occur. Fig.6 (b) shows the activation energy in both the forward and the reverse direction to be nearly the same.

An interesting feature of Fig.6 is that for the ClAlPc device, the deviation in activation energies between forward and reverse bias data is high at low temperature and decreases with increasing temperature. However, for the CuPc device the deviation increases with increasing temperature such that it is high at high temperature.We propose that the deviation in CuPc is due to the kinetic energy imparted to the molecules by the rise in temperature. while that in ClAlPc is due to polarization at low temperature.

Conclusions

ClAlPc and CuPc were purificd twise. using cntertainer sublimation techniques and then thin film devices were prepared by thermal evaporation techniques. Dark current voltage measurements were performed in vacuum, and the activation energy evaluated. From the results we conclude that non-symmetrical moleculcs such as ClAlPc display different activation energies depending upon the direction of the bias voltage. This is due to the molecule being polarized more readily.

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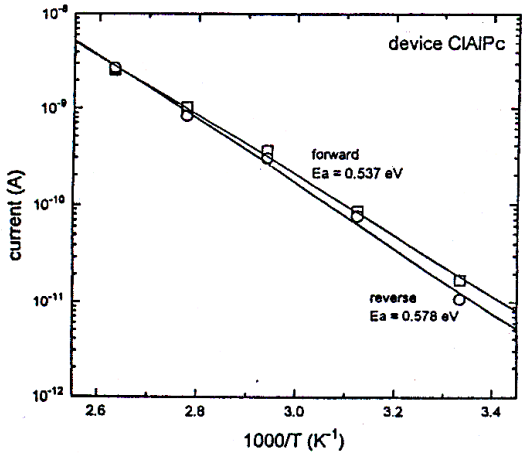


Fig. 6 (a): A semi-logarithmic plot of log I against liT For a CIAIPc device

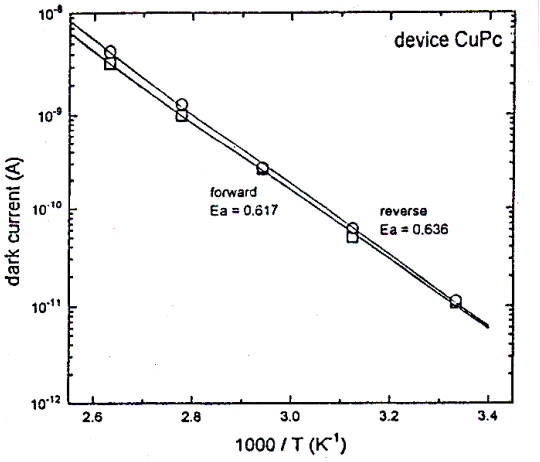


Fig. 6(b): A semi-logarithmic plot of log I against 1/T for a CuPc device

That would a symmetrical molecule such as CuPc and this in turn causes a rotation or movement, of the molecule and hence a change in the conduction path through the lattice.

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