IBN AL- HAITHAM J. FOR PURE & APPL. SCI. VOL.19 (1) 2006

Electrical Characteristics of Planar Phthalocyanine Thin Films

K. A. Mohammed

Department Physics, College of Education Ibn-Al-Haithem, University of Baghdad

Abstract

The electrical properties of thin film interdigital metal-phthalocyanine - metal devices have been studied with regard to purity and electrode material . Devices utilising phthalocyanines (H_2 Pc , NiPc and CuPc) films with Au , Ag , Cu ، In and Al electrodes have been prepared with Pc layers fabricated from both as - supplied Pc powder and entrainer - subcimed material . The results indicate that sublimed phthalocyanine with gold electrodes offers the best material combination with regard to linearity , reversibility and reproducibility. Measurements of current - temperature characteristics of phthalocyanines indicate that the impurity of the film have a major influence on conduction mechanism.

Introduction

The phthalocyanine molecule (Pc) , shown in fig.1 , both metal - free H_2Pc and metal - substituted MPc , have been investigated in the form of both single crystal and evaporated thin films (1 – 3).

In particular , the phthalocyanine class of organometalic compounds has received a considerable attentaion and recently there has been a renewed interest in their properties for device applications (4- 8).

The physical and chemical properties of phthalocyanine (9) make them good candidates for sensing elements in semiconductor gas detectors as most of the reauirements of an ideal sensor (selectivity , sensitivity , reversibility , simplicity and portability) are , or can be , attained with a phthalocyanine based device . In the present work , we give a detailed consideration to the effects of phthalocyanine purity , different electrode materials in interdigital metal - Pc - metal planar devices with aview, to optimizing these towards the fabrication of an ideal sensor . In this paper we consider H_2Pc , Ni Pc and Cu Pc with Au , Cu , In and Al electrodes for pure and entrainer sublimed material.

Experimental

The as – supplied Pcs were in the form of impure β – phase powder.Purification was by means of entrainer sublimation(10) we note , however that the inferion purity of phthalocyanines (impurity concentration of about 1 in 10^{5}) compared to semiconductor grade Si or Ge(impurity concentration < 1 in10^{12}) may not be too significant or perditious that the reproducibility of electrical characteristics can be obtained .Substrates were boropolysilicate glass precleaned sequentially in a cetone vapour , altrasoneration in a degreasing agent, dionised water . Both electrode metals and phthalocyanines were deposited by thermal evaporation in vacuum at a pressure ~ 10^{-5} Torr, electrode thicknsses were about 100 nm and phthalocyanine thickness were typically 150nm . Standard photolithographic techniques were used to produce interdigital electrodes , the Pc being evaporated over the electrode array . Electrical characteristics were measured with devices mounted in a light – tight PTFE chamber shielded with a stainless – steel vacuum vessel . Devices were heated by mounting them on a platinum film heater.

Results

Electrode metal: Fig. (2) shows the d.c dark current – voltage characteristics for typical purified Ni Pc devices with Gold (Au) , Indium a (In) and silver (Ag) electrode . The characteristics were all measured in dry air and in the dark . The charateristics for gold electrodes is seen to be ohmic and has a higher conductivity and more linear , while that for nickle electrodes is clearly non linear over the voltage range studied . The characteristics for indium is also ohmic although the measured current is significantly smaller than that for gold at the same bais . The characteristic for Ag electrodes is also curved and the device resistance is appreciably higher than with gold electrodes .As silver oxidises relatively slowly at room temperature , the presence of an oxide layer blocking contact cannot be assumed to explain the shape of the characteristic .

The IV characteristics of a typical device using copper as electrode material is shown in fig. (3 a) .

The applied voltage was increased 0.1 to 1.0 V and then the device allowed to stabilise for 24 hrs. Considerable current drift (113 % change) occuvred over this period .

The bias was then reduced back down to 0.1V a gain giving the hysteresis effect shown . In the low – voltage region (0.1V) one would expect an ohmic contact to give linear characteristics and therefore one can conclude that the Cu – Nipc contact is non – ohmic over this voltage region . As a comparison , however , the corresponding characteristics of Au – Ni Pc – Au device are shown in fig. (3b). The Ni Pc for the sample shown was deposited during the same run as that in fig. (2a), that is under identical conditions. Over the same voltage range , the characteristic is seen to be linear. There is some hysteresis due to current drift during the stabilization period , but this is much smaller than for the copper electrodes and the characteristic remain linear . In a real sensor this would probably necessitate after each exposure .

The current – voltage for Ni Pc deposited on aliminium electrodes is shown in fig.(4). This organic film was also deposited at the same time as in fig. (3a,b), and the characteristic measured at room temperature . A rough calculation of the resistance of this sample about an order of magnitude higher than for gold electrode devices and were nonlinear over the whole voltage range . This can be understood in terms of an oxide layer interposed between the NiPc – $Al_x O_y$ interface (where $Al_x O_y$ is the oxide layer formed on the Al prior to NiPc deposition) . This is dominant at low fields and has been shown by several authors to form a schottky barrior (11,12). If this is the case, then the current - voltage relationship can be described by the equation .

$$I_D = A \exp\left[\frac{eBE^{1/2}}{KT}\right]$$

where I_D = dark current

A = constant (dependent on barrier height and absolute temperature).

e = electronic charge .

$B = (e / 4 \Pi \in_0 \in_r)^{1/2}$

$\in_0$ = free space permitivity

$\in_r$ = dielectric constant

E = contact field = applied voltage \ depletion width

K = Boltzmanns constant

T = absolute temperature.

Fig. (5) shows aplot of $L_n \, I_D$ against $V_b^{1/2}$ for a device with Al electrodes .One must be careful when treated data using either Schottky emission theory (Field essisted thermoinic emission over surface barrier) or Poole - Frankel emission theory (field essisted thermal detraping of carriers) as the parameter is often not constant . value of $\in_r = 3.2$ have been reported for cupc (13) and we will assume that they apply also to NiPc (14) . However , taking $\in_r = 3.2$ and T = 290 K yields adeplation region width of 25 nm , while is reasonable on the basis of the work of vidadi etal (14) ، and Fan and Faulkner (15) .

Phthalocyanine purity

Using gold as the electrode material the, device characteristics were measured as a function of phthalocyanine purity . This involved using material as obtained directly from the manufacturer (impure β - form powder) and comparing this with the entrainer sublimed material (pure β - form crystals) . Metal free phthalocyanine (H_2 Pc) , cupc and Nipc were used in this study . Dark - cnrrent measurements in dry air showed that the purified material had a higher conductirity and more linear characteristics for all phthalocyanine studied .

The results of a chemical analysis of the sample to determine the percentage composition of carbon , nitrogen , hydrogen and copper (where oppropriate) are given in table (1) and tabls (2) for metal free and copper phthalocyanine , respectively .

The figures in the column lablled " calculated " were determined using the atomic weights 1 - 0079 for hydrogen , 12.0l1 for carbon , 14.0067 for nitrogen and 63.546 for copper . we conclude that the entrainer sublimed material gives ratio much closer to that expected , knowing the molecular weight of the compound studied (H_2Pc = 514.548 a . m .u . and Cu Pc = 576 . 078 a . m . u .) .

Adding the percentage composition for each sample we find that only about 85 % of the impure material is identifiable as Cu Pc or $H_2 P_c$ (from the C , N and H data) . We can only assume that the shortfall is due to inorganic (i . e . not containing C, N or H) impurities , subsequently removed by intrainer sublimation .

Temperature Dependence of the Conductivity

Fig. (6) shows aplot of $I_n I_D$ against ($10^3 / T$) at constant voltage. The conduction obyes a relation of the form $I = Io \exp(- E \backslash 2 K T)$ as normally observed for phthalocyanines . For the cupc , the slopes yield appreciably different conduction activation energies (0.41 eV for pure Cu Pc and 0.63 eV for the impure material) and for H_2 Pc is 0.76 eV for pure H_2 Pc and 0.8 eV for the impure material .

Discussion

During our investigation it has been found that the electrical conductivity of phthalocyanines are influenced by electrode material and purity . The main objective is varying the nature of the metal for the finished device. This metal has to or an ohmic contact with the phthalocyanine thin films measured in terms of a linear IV response . As expected gold gave the most repeatable ohmic contact, this had been well documented and pointed out by earlier workers on thin films (16,17). Aluminium, nickle, and copper gave non-ohmic contacts as deduced from the non-linearity of their IV characteristics . Non-linearity may be introduced into the current-voltage characteristic by the formation of an oxide contact barrier, by the existence of contamination layer on the metal surface prior to deposition of the phthalocyanine film or by impurities in the PC layer . All of these are likely to introduce non-reproducibility as well as non-linearity into the device . As an electrode material indium was found to give good ohmic behaviour. It appeared that semiconducting indium oxide layer on exposure to air, does not effect the CVC of the device . This can be attributed to the thickness of n-type $In_x O_y$ layer causing tunneling in both directions to be uninnibited .Our experimental devices with Al electrode are several order of magnitude less conductive than corresponding devices with gold. Morever, the results indicated that Aluminium electrode or a blocking junction as a result of a blocking Al_x O_y-N_iP_c contact . The existence of Schottky barrier of width (25 nm) is deduced from slope fig.(5) and given ϵ_r=3.2 .Such a value agrees fairly well with the reported thickness for grown insulating layer of Al_xO_y occupies the Al-N_iP_c junction at room temperature (18).

We conclude that the optimum contact material for a sensor is gold with indium as a possible candidate of low resistance is not necessary.The method of preparation and hence, purity of the phthalocyanine has been found to play a siqnificant role in determining device behaviour. It is clear from our results that the presence of impurities effects the resistivity, linearity, hysteris and drift of the electrical characteristics, and also the conduction activation energy and hence the specific conduction mechanism .In the case of CuPc stienbach et. al. 1975 (19) have suggested that the observed behaviour (enhanced sorption for impure films), is due to an electron density change associated with Cu atom in the Cu Pc molecule due to strong π-electron interaction between the CuPc molecule and the incorporated impurities. Our studies with several phthalocyanines showed similar results. Dark-current conductivity measurement on devices prepared with as supplied Pc's (impure) and entrainer sublimed material (pure), in dry air, showed that the purified material had higher conductivity and more linear characteristics. Additionally, conductivity-temperature measurements have yielded conduction activation energy values of typically higher for the impure than that for purified material. There is an inconsisty between the activation energies for the purified and impurified material .If the carrier excitation is occruing from impurity levels between the valence and conduction bands then, assuming that these are the defect levels removed on purification we would expect an increase in the activation energy after purification this is not observed. The impurities removed are probably volatile low-boiling point organics whereas it is likely that inorganic impurities, for example other metals are influencing the conduction mechanism.Most likely of all we are dealing with trapping levels in the bulk of the thin film, this is verified by the non-ohmic behaviour of unpurified devices.

References

1.Gutmann, F.; Keyzer,H. and Lyons, L. E.(1983) Organic semiconductors (florida : krieger) part B .

2. Vartanyan, A . T . (1974) . Acta physiochem .USSR 22 :201-224.

3. Gould, R.D. (1985) Thin Solid Films 125 : 63-69.

4. Hassan, A.K. (1998) "The effect of on optical absorption in langmuir –Blodgett films of octasubstituted amphiphilic copper phthalocyanine molecules" Sensors and Actuators B-Chemical, 49 :235-239.

5. Loutfy, R.O.; Sharp, J.H. and Hsaio, C.K. (1981) phthalocyanine organic solar cells.Indium /x –metal free phthalocyanine schottky barriers". J.Appl.Phys.,52: 5218-5230.

6. Twarowski, A. (1982) " Temerature dependence of the schottky barrier capacitance in α - and β -zinc phthalocyanine " J.Chem.Phys.,77 : 4698 – 4703.

7. Gould, R.D. and Shafai, T.S. (1999) "Conduction in lead phthalocyanine thin films with aluminium electrodes " Superficics Y Vacio, 9 :226-229.

8. Honeybourne, C.L. ; Ewen, R.J. and Hill, C.A.S. (1984) " use of thin films of conjugated organic macrocycles as the active element in toxic – gas sensors oprating at room temperature ". J. Chem .Soc .Faraday Trans ., 1 : (80) 851 –863.

9. Moser, F.H. and Thomas, A.L. (1983) "The phthalocyanines" vol.1 C.R.C . Press, Boca Raton.

10. Ferguson, J. (1957) "Migration of excitation energy in organic crystals " Aus. J.Chem., 9: 160-171.

11. Collins, R.A. and Mohammed, K.A. (1986) "Electrical , Structural and Gas Sensing Properties of Zinc Phthalocyanine Thin films" Thin Solid Films, 145: 133 –145 .

12. Hassan, A.K. and Gould, R.D. (1992) " Space charge limited conductivity and trapping mode diagnosis in thin films of nickel phthalocyanine". Int .Electronics, 13: 1047 –1049.

13. Vidadi, Yu. A. (1976) "Direct conductivity of copper phthalocyanine films in the presence of blocking contacts ". Phys . Stat. Sol.(a) 33: k67-71 .

14. Vidadi, Yu. A. ; Sadraddinov, S.A. and Zeinally, A. Kh. (1982) "Frenkel –poole effect in phthalocyanine" Sov. Tech. Phys .Lett, 8: 133 –134.

15. Fan, F.R. and Faulkner, L.R. (1978) "Photovolataic effects of metal free and zinc phthalocyanine". J.Chem . Phys., 693341- 3349.

16. Kaneto, K.(1976) "Electrical conduction in epitaxial films of phthalocyanines " Technol . Report . Osaka University , 26: 1276 – 1307 .

17. Cox, G.A. and Knight, P.C. (1973) "Electrical conduction mechanism and carrier trapping in β - metal free phthalocyanine single crystals " J.Phys. Chem .Solids 34: 1655 –1659.

18. Hackham, R.H. and Harrop, P. (1972) Solid . State . Electron . 15: 1031.

19. Stienback, F.; Schmidt, H.H. and Zable, M. (1975) Proc .Int .symp .Relation between Hetrogeneous and Homogeneous catalytic phenomena (Brussels) 1974 (Amsterdam : Elsevier) p. 417 .

Table (1) Chemical anayslis of H_2 P_c

β- H_2P_c	calculated	determined	
C (Wt %)	74 . 70	74 . 85 *	64 . 10**
N (wt %)	21 . 78	21 . 45	18 . 04
H (wt %)	3 . 52	3 . 13	3 . 41

* Entrainer sublimed

** As obtained from manufacturer

Table(2) Chemical analysis of Cu Pc

β - Cu Pc	calculated	determined	
C (W t %)	66 . 72	67 . 37 a	56 . 80 b
N (W t %)	19 . 45	19 . 39	16 . 45
H (W t %)	2 . 80	2 . 40	2 . 72
Cu (W t %)	11 .03	9 . 79	8 . 3

a) Entrainer sublimed

b) AS obtained from manufacturer .

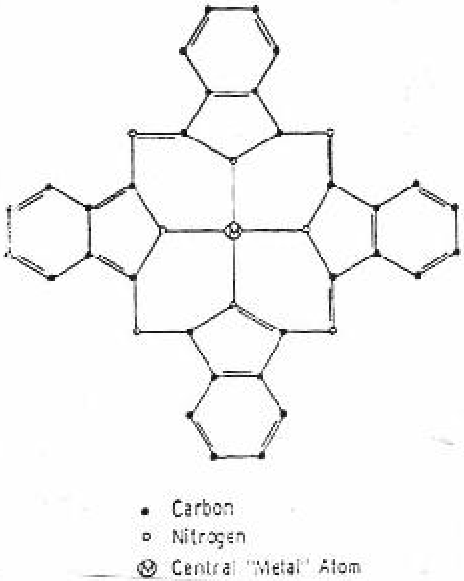


Fig. (1) The phthalocyanine molecule .

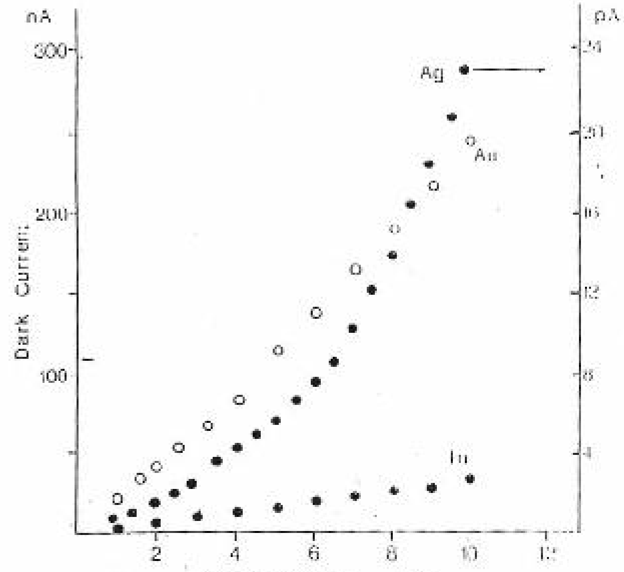


Fig. (2) D.C dark current – voltage characteristics for NiPc devices Ag, Au and In electrodes .

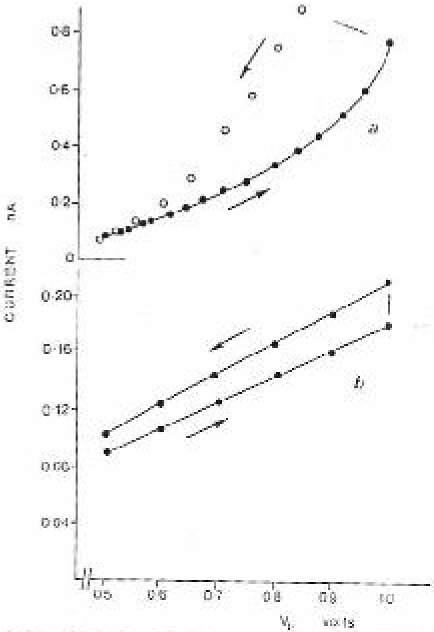
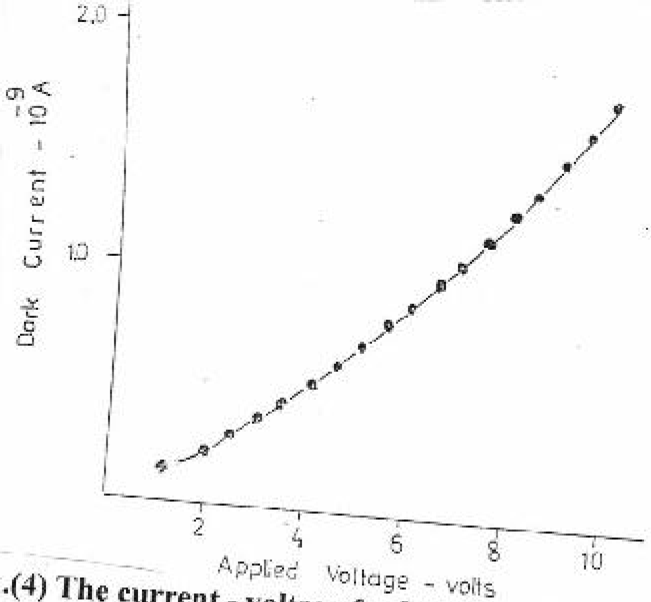


Fig. (3) Dark current – voltage characteristics for NiPc devices with (a) Cu and (b) Au electrodes .



Figu.(4) The current - voltage for NiPc deposited on Al electrodes .

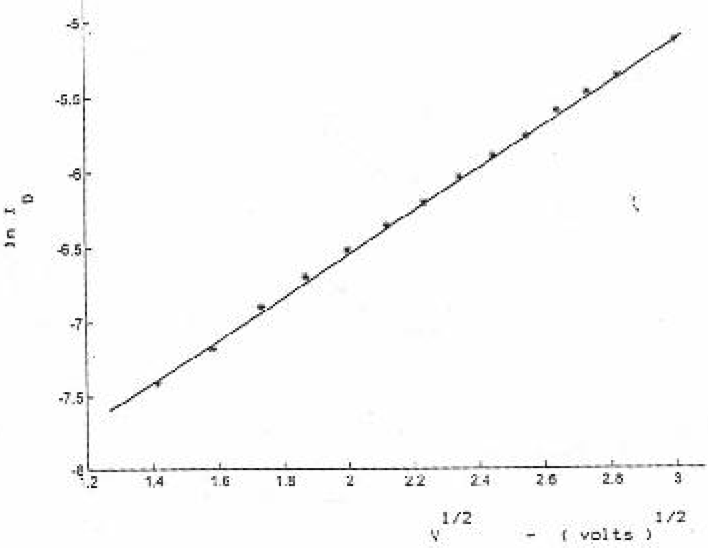


Fig. (5) Plot of ln (dark current)- (applied voltage) $^{1/2}$ for a NiPc device with Al and In electrodes .

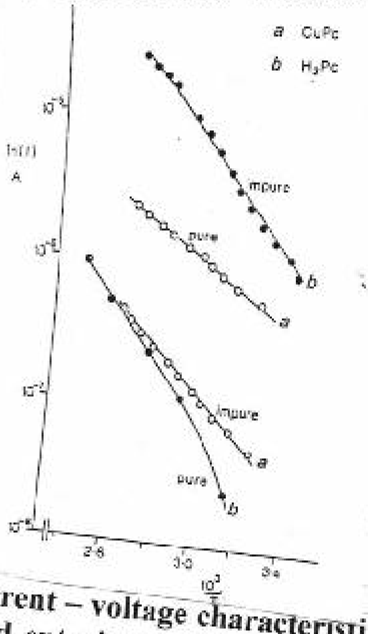


Fig. (6) Dark current – voltage characteristics for both impure and entrainer sublimed Pc devices using (a) CuPc (b) H_2Pc

الخصائص الكهربائية لاغشية الفيثالوسيانين المستوية الرقيقة

قاسم عزيز محمد
قسم الفيزياء، كلية التربية – ابن الهيثم، جامعة بغداد

الخلاصة

تم دراسة الصفات الكهربائية لاغشية معدن – شبه موصل – معدن نسبة الى الشوائب الموجودة في هذه النبائط وتأثير النقاوة على سلوكها فضلا عن تأثير نوع القطب المستخدم . ثم تم دراسة النبائط المستعملة والمصنعة من مصادرها او بعد تنقيتها وقد وجد ان نسبة نقاوة شبه الموصل تعطى نوعية عالية الجودة من الاستقامة في الخصائص و كذلك عالية الانعكاسية والاستقرارية فضلاً عن تأثيرها على ميكانيكية التوصيل لهذه الانواع من النبائط .