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METAL COMPLEX TETRAIZOINDOLES AS SENSOR MATERIALS

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ABSTRACT

The paper presents the synthetic routes for obtaining of some organic semiconductors and their characterization in order to use in thin film deposition for gas sensing devices.

An original technique was used to control the molecular weight of polymeric phthalocyanine.

We have fabricated devices consisting of evaporated thin films of copper, nickel and iron phthalocyanines onto interdigital electrodes and estimated the electrical conductivity by in-situ measurements. The films were evaporated onto substrates (gold or aluminum) which were entirely integrated in the standard CMOS (capacitor metal oxide semiconductor) technology.

The objectives of this work were to improve the synthesis methods of organic metal-complex tetraizoindoles and their polymers and to evaluate their electrical response and thermal stability as evaporated thin films. We have also investigated the variation of polymers conductivity and sublimation yield with the average molecular weight. We found that for polymeric phthalocyanines, the thermal stability was higher than for Pcs monomers. The stability of polymers increased with the average molecular weight.

Keywords: organic semiconductors, phthalocyanine, polymers, electrical measurement, thermal stability.

RESUMO

Este trabalho trata da síntese e propriedades de películas finas de ftalocianinas de Cu, Ni e Fe. Em particular, foram determinadas propriedades tais como peso molecular, estabilidade térmica de ftalocianinas poliméricas, condutividade in- situ. As películas foram evaporadas sobre substratos de Au ou Al completamente integrados na teconologia CMOS. A condutividade elétrica está relacionada ao tamando do sistema conjugado de eletrons -π e os gases adsorvidos sobre os filmes finos.

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1. Introduction

Monomeric and polymeric compounds of metallic phthalocyanines (MePcs) are of great interest in material science because of their electronic and photophysical properties. The use of these materials is expected to significantly increase the performance of gas detection devices for NO, NO_2, CO, NH_3, and other gases. MePcs are proved to be organic semiconductors; the majority of carriers in double sublimated CuPc are p-types carriers [1].

One of the best-known molecules in cell signaling is nitric oxide (NO). It has a wide range of functions including regulation of blood pressure and neurotransmission. Since its half-life is very short (in range of seconds), devices detecting small amounts of NO have to be enough sensitive to overcome such difficulties. Solid MePc (Me=Mn, Co, Cu, and Fe) have been reported to axial coordinate NO [2]. The coordination between the central metal and the NO molecule was accompanied by some electron transfer phenomena.

Thin films of PbPc (lead phthalocyanine) have been shown particularly sensitive to NO_2, with useful response to Cl_2 and very low sensitivity to electron donor gases. For reversibility and minimized effects of water vapor, most of the work on these devices has been carried out at 100^0C. The film sensitivity decreases with the increasing of temperature above 160^0C, because of strong adsorption and reaction of oxygen with the lead atom.

In metal-free, NiPc or FePc there is no evidence of a similar process[3]. PbPc, NiPc and CuPc show significant changes in IR adsorption spectra following high-temperature ($>300^0C$) treatment. These changes are consistent with the modification in polymorphism of Pcs from the α-phase to the β-phase (for CuPc and NiPc). For PbPc, which has no α or β polymorphism, the observed properties seem to be due to the non-planar structure the single crystal.

Evaporated thin films of CuPc exhibit reversible changes of conductance in the presence of very small (ppb) concentrations of oxidizing gases: NO, O_3, SO_2, etc. The conductance of films didn't change after exposing them to reducing gases as CO [4].

2. Materials and Methods

We succeeded in synthesizing several MePc, monomers and polymers. The synthesis procedures for monomers were previously presented in detail[5]. The MePc monomers were obtained either by classical synthesis methods (in solvent, at high temperature), or by using a better method (without solvent, in a microwave field).

We prepared MePcs (Me = Cu, Co, Ni and Fe (II) in a microwave field by heating phthalonitrile with metal salts and urea (using a molar ratio 5:1:5) for 15 minutes at 220^0C. The magnetron power was 500-600W.

A new method was used for purifying the monomers. The crude solid product was added into 40ml acetonitrile and the suspension was heated under reflux for 30 minutes. After cooling the solid is filtered off, washed with distilled water and purified again with HCl 2% solution and NaOH 2% solution.

The second technique has been shown to be faster and more efficient than the classical techniques.

The polymers were prepared by the reaction of pyromellitic anhydride, urea and metal salts (using a molar ratio of 1:20:1.5) at 180-200^{0}C for 5 minutes.

An original method was applied to obtain polymeric MePcs with variable average molecular weight (MW). The structure is presented in figure 1. In order to stop the polymerization, variable amounts of phthalic anhydride were added to the usual reaction mixture. The molar ratio between pyromellitic dianhydride and phthalic anhydride was in the range of 1:0 to 1:0.9.

We obtained a variation of the average molecular weight between 4.000D and 80.000D.

Characterization of the Pcs

The elemental analysis of the Pcs confirmed a high purity degree of synthesized compounds. The results, including IR and UV-VIS analysis, are reported in tables 1 and 2. The polymers are dark blue-green to black powders with fair thermal stability and show the visible and infrared absorption bands, characteristic of phthalocyanines.

The thermal behavior of Pc products appears to be the key for their use in evaporated thin films (stability to high-temperature treatment, sublimation capacity, etc.).

The thermogravimetrical analysis (TGA) was carried out on TGA-V5-1A Du Pont 2000 equipment. Thermal evaporation was carried out at 200-400^{0}C and 2x10^{-5} mbar for 60-90nm thickness of monomers Pcs. For polymeric Pcs, higher temperatures were required (>1000K), with a step rate of 200K/min. The layer to be obtained was about 30 times thicker (300nm).

The SEM pictures of the evaporated thin films were obtained using a scanning electron microscope Philips XL 20.

The thin film preparation

All of the Pc thin films were obtained by vacuum evaporation, using a Bal-Tech Med 020-Modular high vacuum coating system. Each of tested Pcs was deposited onto an electronic device using a mask. For each deposition, approximately 2g of Pc powder was evaporated from a molybdenum boat, at high temperature (300-400^{0}C), under a vacuum pressure of 8.7x10^{-5}mbar. The geometry of the films was determined by the mask pattern.

Using a deposition rate of 0.20nm/s for all the Pcs (NiPc, FePc and CuPc), films of 20-40nm thickness were obtained. The deposition was controlled with a film thickness and rate monitor **QSG 060, BAL-TEC** type (Liechtenstein). For polymeric Pc higher temperatures were required (>630^{0}C).

Phthalocyanine films were evaporated onto the substrates of the interdigital electrodes in order to analyze their sheet resistivities. The Pc film temperature was accurately controlled by the integrated heating element and thermoresistor. For an accurate deposition of phthalocyanine in the active area of the device, the lift off technique was used. The active area of the sensor contained the metal electrodes. The thickness of the metal layer (Cr-Au) was 400nm.

The process for obtaining the interdigital integrated sensor was presented in detail elsewhere[6].

Table 1. **Metallic Phthalocyanine characterization**

Nr. crt	Pcs	Elemental analysis								IR values (KBr)	UV-VIZ values (DMF)	
		C%		H%		N%		Metal %		-cm^{-1}-	λ_{max} (nm)	lg ε
		requires	found	requires	found	requires	found	requires	found			
1	CuPc	66.74	66.69	2.78	2.72	19.45	19.41	11.03	11.00	728, 754, 779, 874, 894, 1048, 1081, 1114, 1157, 1277, 1324, 1409, 1452, 1495, 1602, 3025	662	0.495
2	CoPc	67.28	67.30	2.80	2.79	19.61	19.57	10.32	10.28	733, 736, 756, 780, 870, 910, 1056, 1089, 1118, 1157, 1283, 1327, 1419, 1458, 1515, 1591, 3040	646	0.628
3	NiPc	67.30	67.27	2.80	2.75	19.61	19.57	10.27	10.25	727, 752, 771, 861, 907, 1055, 1084, 1114, 1157, 1277, 1320, 1415, 1457, 1517, 1596, 3025	655	0.775
4	FePc (II)	67.64	67.59	2.82	2.78	19.71	19.67	9.83	9.78	734, 56, 780, 871, 904, 1076, 1117, 1156,1279, 1327, 1411, 1456, 1501, 1598, 3035	587 645	0.507 1.407

Table 2. **Copper polyphthalocyanine characterization and mean molecular weight variation**

Polymer no.	Molar ratio pyromellitic anhydride: phthalic anhydride	% CuFt* monomer	Elemental analysis				VIS	Solubility (g/100ml DMF)	Viscosity
			N%		Cu%		λ_{max} (nm)		
			requires	found	requires	found			
1	1:0	0	20.41	19.13	11.56	3.84	667, 641, 603	0.003	1.84
2	1:0.1	0.5	20.41	15.09	11.56	3.84	692, 685, 658	0.003	0.19
3	1:0.3	2	20.41	17.52	11.56	13.66	667, 640, 602	0.007	0.38
4	1:0.5	2.6	20.41	18.5	11.56	3.8	698, 650, 610	0.006	0.56
5	1:0.6	4	20.41	15.02	11.56	4.32	670, 650, 603	0.007	0.507
6	1:0.7	8	20.41	19.35	11.56	15.21	667, 639, 602	0.009	0.83
7	1:0.8	11	20.41	22.25	11.56	14.77	668, 639, 602	0.014	0.65
8	1:0.9	14	20.41	17.81	11.56	9.2	668, 639, 601	0.1	1.58

** found by extraction of polymer in basically solution (DMF-water)*

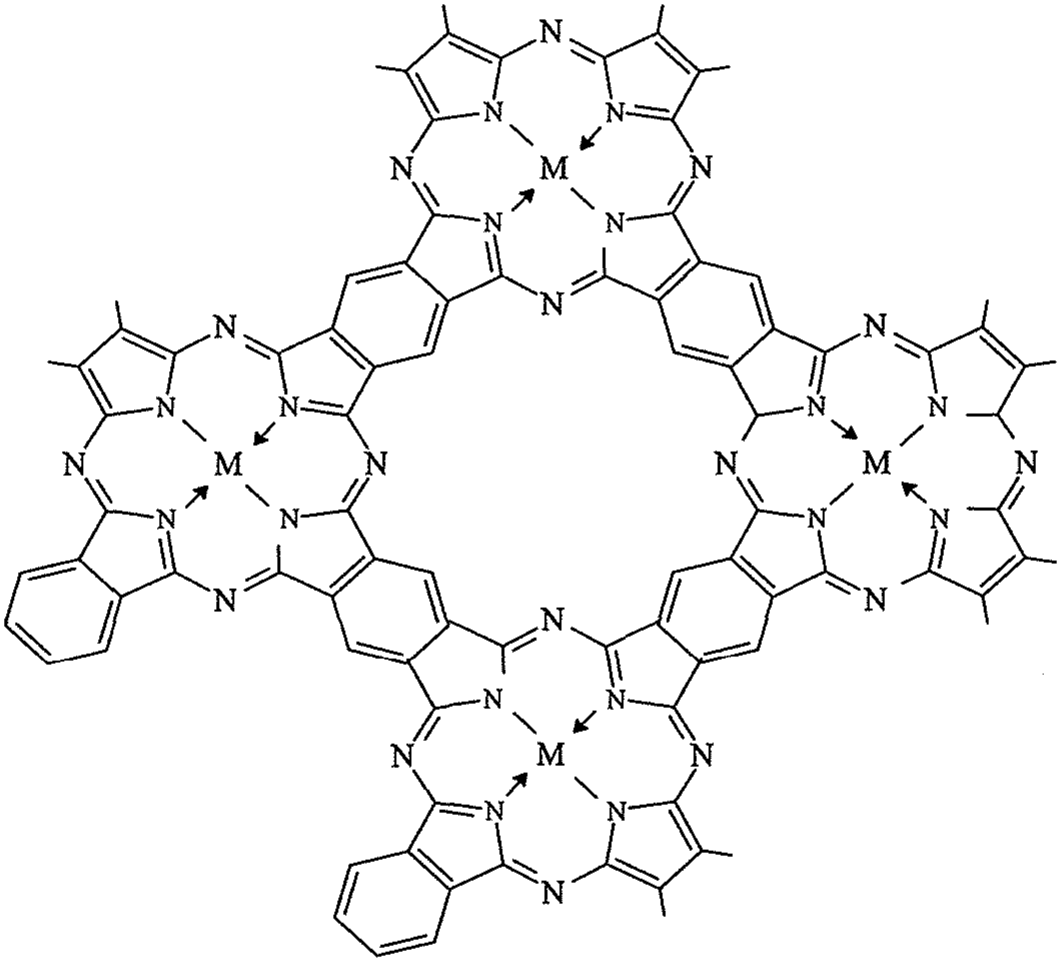

Fig.1. Metallic phthalocyanine polymer structure

3. Results and Discussion

CuPc monomer exhibited a remarkable thermal stability up to 300°C. After this point, the sublimation process was very fast with a constant rate of evaporation (0.16nm/s.) and a minimal decomposition of the CuPc (<1%).

For the polymeric phthalocyanines, the thermal stability was higher than for Pcs monomers. The stability increased with the average molecular weight (350°C for MW = 20.000D and more than 600°C for MW = 80.000D). The polymeric pigment stability was not dependent on observed temperatures between 125-400°C. The molecular weight decrease up to 125°C was due to the humidity loss.

Electrical conductibility was determined for CuPc ($10^{-12}\Omega^{-1}cm^{-1}$) and for polymeric Pcs ($5x10^{-2}\,\Omega^{-1}cm^{-1}$ when MW = 80.000D).

For a variation of molecular weight in the range of 4.000D and 80.000D, the specific resistivity was $\rho=10^{-9}$- $5x10^{-2}\Omega^{-1}cm^{-1}$ as shown in figure 2.

The ρ variation with the temperature is exponential:

$$\rho = \rho_0 \cdot e^{\varepsilon/2kT}$$

where: ρ_0 - specific resistance at very high temperature (infinite), ε - width of restricted band, k - Boltzmann constant.

$$\ln\rho = \ln\rho_0 + \varepsilon/2kT$$

The Pcs films deposited onto microsensor electrodes had high resistance values: 10MΩ for CuPc, 15MΩ for NiPc and 30MΩ for FePc. It is important to study the uniformity of the resulting layers in order to prevent degradation by clustering of the contact metal. The electrode strips were thicker than the Pc film deposited on the top. A relative bad covering of the strips and a relative high number of cracks caused by the edges of the capacitor strips were expected. Pcs did not form a continuous film over the edge of the electrode strips.

During the evaporation, the incident angle of the Pc molecules was not normal to the surface and, therefore, the strip edge formed a kind of shadow on one side. The cracks can be observed in SEM picture of the electrodes covered with MePc layer (figure 3).

In very aggressive environments, MePc films were very stable and still sensitive to gases. The films were evaporated on interdigital electrode substrates (gold or aluminum) which were entirely integrated in the standard CMOS (capacitor metal oxide semiconductor) technology for detection of NO, NO_2 in the air.

4. Conclusions

The conductance of very thin films allowed resistance measurements without any contact problems. The electrical conductivity dependence to the adsorbed gas nature was correlated with the size of the π electron-conjugated system in the polymeric molecules.

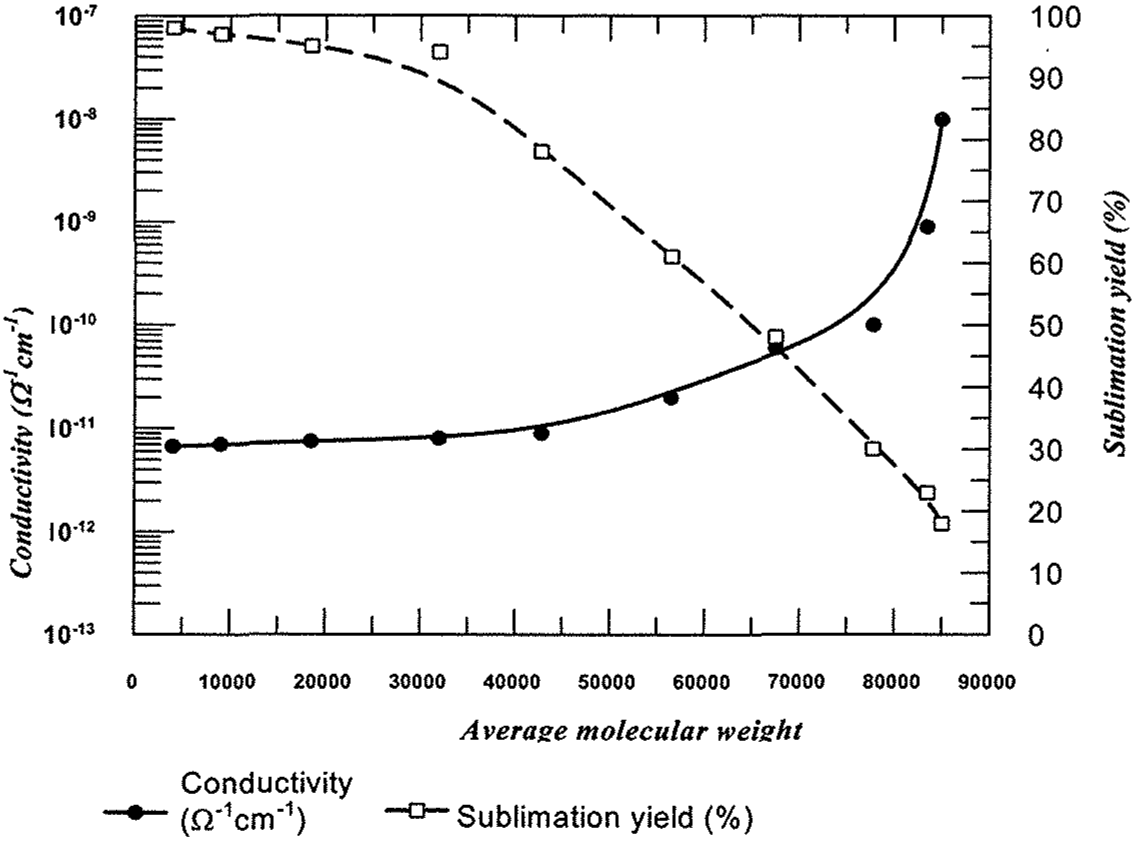

Fig.2. Variation of polymers conductivity and sublimation yield with the average molecular weight

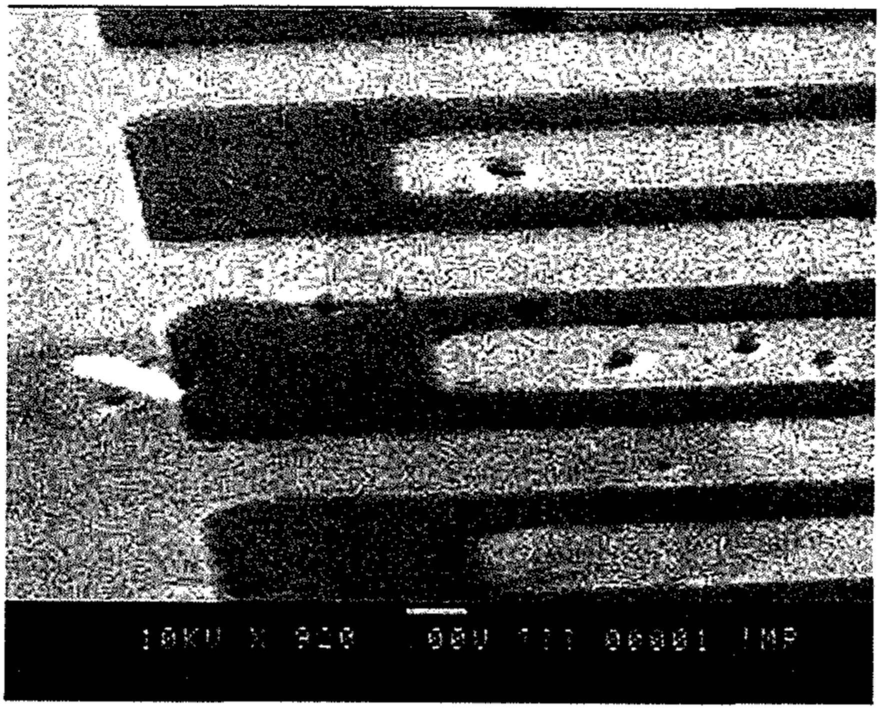

Fig 3. SEM picture of electrodes covered with 20nm FePc thin film

However, resistance to sublimation decreased with the increasing of the average molecular weight. The decrease was more significant under molecular weights of 50.000D.

This behavior of Pc requires further research in order to achieve a more reproducible technology for producing highly sensitive detecting layers, in gas sensors.

5. References

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