

TOWARDS A NEW GAS SENSOR MICROSYSTEM USING ELECTROACTIVE POLYMERS THIN FILMS

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Abstract- This paper describes the development of a new gas sensor device using some electroactive polymers in thin layers. The poly(fluoro-aluminium phthalocyanine) powder, (AlPcF)_n, has been synthesized, then deposited by vacuum evaporation on alumina or silicon substrates in the form of thin films with control of the deposition rate. (AlPcF)_n thin layers are doped by NO₂ or O₂ diluted at various concentrations in N₂ and their conductivity variations are studied as a function of time, temperature and doping gas concentration. The doping process is reversible, and the experimental results are interpreted in terms of adsorption and diffusion of the gas in the polymer, charge transfer, and transport of the injected carriers in the polymer chain.

These experimental results and previous studies on other polymers and oxidizing gases demonstrate the potentiality of such materials to be used as sensitive part of gas sensors.

Index terms: Phthalocyanines, thin films, conductivity variations, gas concentration, doping, adsorption, diffusion, reversibility, charge transfer, gas sensor, air pollution.

I. INTRODUCTION

Because their chemical and physical properties may be tailored over a wide range of characteristics, the use of polymers is finding a permanent place in sophisticated electronic measuring devices such as sensors [1-5]. During the last twenty years, polymers have gained tremendous recognition in the field of gas sensing [6, 7] where better selectivity and rapid measurements have been achieved by replacing classical sensor materials with polymers involving nanotechnology and exploiting either the intrinsic or extrinsic functions of polymers.

Electroactive polymers are generally insulating or semiconducting with a wide gap in their pristine state, but these materials may have their electrical conductivity enhanced by several orders of magnitude when they are exposed to oxidizing or reducing agents (dopants). This comes from the charge transfer between the polymer and the dopant and the mobility along the conjugated polymer chains of the so-injected charge carriers. Since the doping of some polymers may be achieved by electrons acceptor or donor gases, the subsequent increase in their conductivity could be related to the gas concentration, and so the use of these materials as sensitive element of gas sensors could be possible [8, 9].

With this aim in mind, we have performed various dopings with oxidizing gases (particularly NO_2 and O_2) on the poly(fluoro-aluminium phthalocyanine), $(\text{AlPcF})_n$, and interpreted the results with the help of theories on gas adsorption and diffusion in solid and on conduction processes in electroactive polymers. $(\text{AlPcF})_n$ has been chosen because of its high air and thermal stability, its sensitivity to oxidants and its capacity to be sublimated and therefore deposited as thin layers on convenient substrates.

Thin films have also been chosen because of their compatibility with microelectronics and consequently the possibility of miniaturization, mass production, reproducibility of the geometry and reduction of the sensor response time [10].

II. MATERIALS AND METHODS

II.1. Generalities about gas sensors development:

A chemical sensor in general, and a gas sensor in particular, allows direct translation of the concentration of a chemical entity into an electrical or optical signal. This can be inserted in a signal-processing unit to obtain the recognition of a particular gas and to give its concentration. The sensor is devoted to real-time measurement of the gas in a gaseous or liquid environment. A chemical sensor is constituted of a part allowing the chemical recognition associated with a transducing system. The detection principle is based on interactions between the sensitive layer of the sensor and the target gas giving rise to an ionic or electronic exchange, or any other electrostatic effect. Two main classes of materials can ensure this recognition:

- metals and semiconductors giving electronic exchange
- ionic conductors giving ionic exchange.

The methods of measurement involve amperometers, potentiometers and resistance monitoring. Strong demands for chemical sensors, especially for gas sensors, are now expressed in environmental, security and biomedical domains, and in the industry of chemical processes. General public applications like domestic and automotive ones need implementation of gas sensors in industry. Only three sorts of gas sensors using materials in solid phase lead to industrial developments:

- catalytic sensors
- electrochemical cells sensors
- semiconductors sensors.

Catalytic sensors are miniature calorimeters used to measure the energy released during oxidation of combustible gas. The sensing element is made up of an oxide with great specific surface provided by a metallic catalyst in which a platinum wire is inserted. This wire is not only the heating system operating up to appropriate temperatures (between 500 and 800°C) but also the transducer of the sensor structure. Indeed, its resistance value is related to changes of temperature caused by oxidation of inflammable gases. Those sensors need oxygen to work and they present a weak selectivity because they are sensitive to almost all of the hydrocarbon species. Historically, catalytic sensors were the first sensors developed on industrial scale at the beginning of the sixties. They were mainly used in safety-control applications to detect methane gas.

Electrochemical cells sensors imply one or several ionic conductors inserted between two membranes. The target gaseous species are in equilibrium with mobile ions of the surface exposed to outdoor air. When there is a modification of the concentration of the active species at the surface of the membrane exposed to atmosphere (i.e., consumption of oxygen atoms for an oxide), there is a displacement of charges and then production of an electric field between surface and bulk. Equilibrium is reached when diffusion forces, caused by species gradient, become equal to electric forces resulting from diffusion. The second membrane non-exposed to the gas is interacting with a chemical reference, which is often constituted by a solid electrode. In such a structure, the concentration of external gas is related to the electrochemical force measured. A lot of sensors constituted by such electrochemical cells are used to detect many gases like O₂, CO, NO, NO₂, SO₂, Cl₂, NH₃, HF, ... For example, they are used to obtain the regulation of combustion engines [11]. However, in such gas sensors, the detection threshold is

often in the range of several parts per million (ppm). They are used in safety detection, but their detection threshold is a limitation of their using in polluting gas sensor monitoring.

Semiconductor gas sensors are made of materials which electrical resistance may be related to the presence of the gas in the environment. Some metallic oxides, like tin dioxide, show good characteristics in this context. In fact they present:

- a sufficiently important electrical resistance under pure air, but low enough to be easily followed by classic apparatus
- an interesting relative variation of electrical resistance under gases.

The nature of the sensing metallic oxide is related to the gas to be detected, but tin dioxide is the more often used material. The chemical composition of this sensing material is affected by departure from stoichiometry, which induces an n-type semiconductor character. The adsorption of a reducing gas, i.e., an electron donor, induces an increase of the electrical conductivity. The more common case is the detection of a reducing gas (CO, H₂, CH₄, hydrocarbons ...) in air, i.e., in an oxidizing environment. In the same way, a p-type semiconducting oxide would be used for the detection of an oxidizing gas.

II.2. Sensing requirements:

The potentially detectable gases are these ones able to induce reversible reactions with molecules of the sensing layer. The information delivered by the sensor is pertinent if the variation of the signal is a reliable image of the variation of the gas concentration. In consequence, the reaction between the gas and molecules of the sensing layer should be reversible; the complex (sensitive site / adsorbed molecule) involved should not be too stable to ensure a fast reversibility of the sensor response. However, this criterion is reached to the detriment of sensitivity of the detection. Working temperature is often used to optimize the different sensors parameters as response time, sensitivity, reversibility, reliability and reproducibility.

An increasing interest for electroactive polymers has developed since it has been demonstrated that these materials, which are generally insulator or semi-conductor in their pristine state, may have their electrical conductivity enhanced by several orders of magnitude when they are exposed to oxidizing or reducing agents (dopants). This comes from the charge transfer between the polymer and the dopant and the mobility along the conjugated polymer chains of the so-injected charge carriers.

(AlPcF)_n has been chosen because of its high air and thermal stability, its sensitivity to oxidants and its capacity to be sublimated and therefore deposited as thin layers on convenient substrates.

II.3. Synthesis of (AlPcF)_n thin films :

The poly(fluoro-aluminium phthalocyanine), (AlPcF)_n, is chemically stable in normal ambient atmosphere, is sensitive to many oxidizing gases without destruction (its ionization potential is 4.55 eV) and can be sublimated. The (AlPcF)_n molecule consists of a linear Al-F- backbone surrounded by a sheath of Pc macro-cycles separated from each other by 3.6 Å (Figure 1).

The (AlPcF)_n powder is synthesized according to the method of Kenney and al. [12].

Thin films of (AlPcF)_n (300 or 2500 Å thick) are elaborated by vacuum evaporation of this powder with control of the deposition rate (2 or 20 Å/sec).

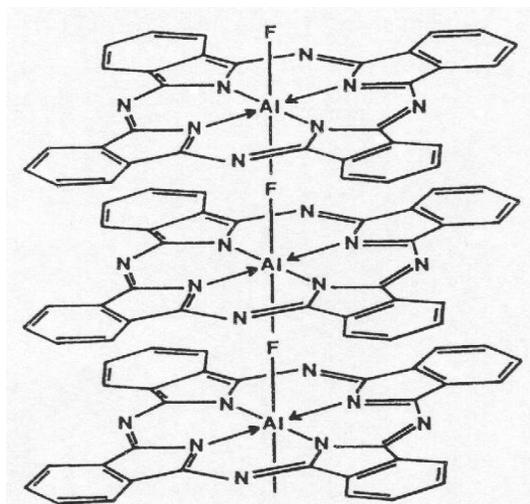


Figure 1. Molecule of (AlPcF)_n

These layers are characterized by IR and UV spectroscopy (which give the same spectra as those published for the (AlPcF)_n powder [13]) and by X-ray diffraction [14].

II.4. Experimental devices:

For doping experiments, the (AlPcF)_n thin films are deposited on two kinds of heatable substrates (dimensions = 3 mm × 5 mm, thickness = 0.3 mm):

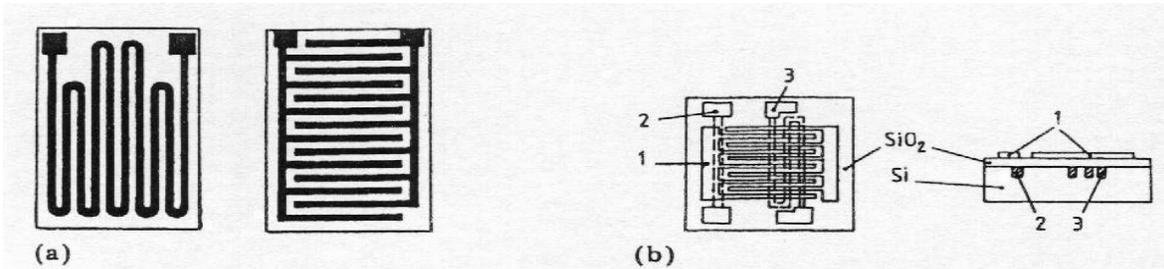


Figure 2. (a) Heatable alumina substrate with platinum screen-printed heater (left) and electrodes (on the right)
 (b) Si and SiO₂ microelectronic heatable substrate. Left : top view; right: section, with 1=electrode, 2=thermometer resistor, 3=heating resistor.

a) Alumina substrate (Figure 2(a)) with, on one side, interdigitated screen-printed platinum electrodes used for σ_{DC} polymer conductivity measurements. On the other side is a screen-printed platinum resistor used both to control and measure temperature.

b) Silicon substrate (Figure 2(b)) with metallic interdigitated electrodes for σ_{DC} measurements isolated from the substrate by a SiO₂ film. Thermometer and heating resistors are obtained by ion implantation.

The oxidizing gases (O₂ or NO₂) are diluted in nitrogen at various concentrations for the ‘doping’ phase, and pure nitrogen is used for ‘dedoping’. The gas flow is injected into a stainless steel cell containing the sample to test.

The sensor structure is polarized under 5V dc and a data acquisition system (Model 2000 or 2700, Keithley) records a voltage as a function of the electric current passing through the sensitive layer, image itself of (AlPcF)_n conductivity [15].

III. EXPERIMENTAL RESULTS

III.1. Undoped (AlPcF)_n :

In a pure nitrogen flow, the room temperature conductivity of a thin layer is :

$$\sigma_{RT} \approx 5.10^{-5} (\Omega.cm)^{-1}$$

Between 190 and 390 °K, the conductivity varies as :

$$\sigma = \sigma_0.exp(-E_a / kT), \text{ with the activation energy } E_a = 0.24 \text{ eV.}$$

The relatively high value of σ_{RT} and low value of E_a compared to the theoretical intrinsic gap are probably due to the presence of impurities (i.e. O_2 , because the layers were kept in ambient air before use).

Heating the layer at about 240 °C makes the conductivity decrease to $\sigma < 10^{-8} (\Omega.cm)^{-1}$ without destruction of the polymer [16, 17].

III.2. Oxygen doped (AlPcF)n :

Only high oxygen concentrations (over 10^4 ppm) may induce noticeable effects on the conductivity.

Figure 3 shows a two orders of magnitude change in σ_{DC} for some cycles of successive pure O_2 ‘doping’ and N_2 ‘dedoping’ when the substrate temperature is regulated to 200 °C.

This substrate temperature plays an important part in σ_{DC} sensitivity for a constant oxygen concentration (Figure 4): a maximum in σ_{DC} is observed at about 160 °C for 10^4 ppm O_2 . The temperature of this maximum is slightly concentration dependent and increases with it: 160 °C for 10^4 ppm, 180 °C for 10^5 ppm and 190 °C for 5×10^5 ppm. From these results, it is obvious that we have to operate near 180 °C to optimize the sensitivity.

This temperature was therefore chosen to test the σ_{DC} dependence of the oxygen concentration C .

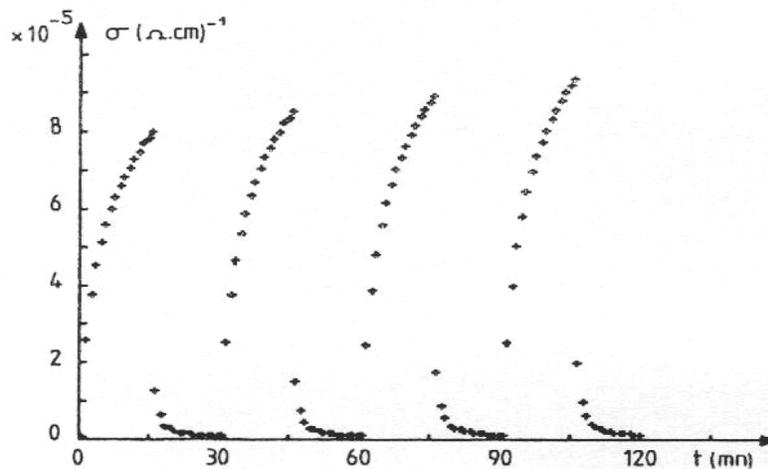


Figure 3. Conductivity vs. time for O_2 ‘doping’ and N_2 ‘dedoping’ at 200 °C.

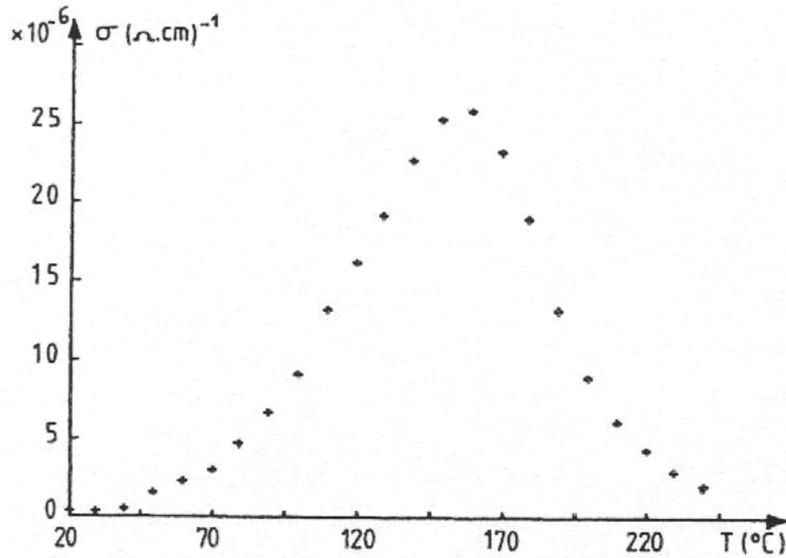


Figure 4. Conductivity vs. temperature for 10^4 ppm O_2 .

As plotted on Figure 5, the experimental results are well fitted by the law :

$$\sigma_{DC} \propto C^{0.54}$$

in the small investigated concentration range $10^4 - 8 \times 10^4$ ppm.

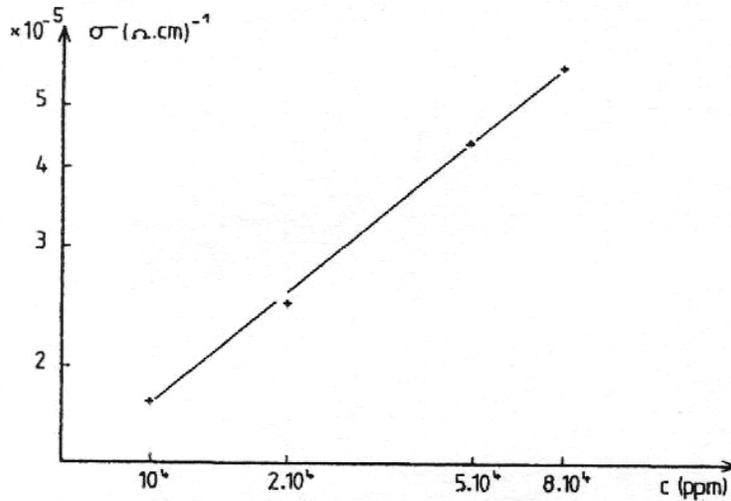


Figure 5. Conductivity vs. O_2 concentration in N_2 at $180^\circ C$.

III.3. Nitrogen dioxide doped (AlPcF)n :

In contrast to the oxygen effect, very low concentrations of NO_2 (of the order of 1 ppm) induce noticeable changes in (AlPcF)n conductivity. At a constant temperature, the conductivity increases with NO_2 concentration: in the range 0-200 ppm, it is proportional to $C^{0.1}$ at $T = 150^\circ C$.

If the temperature is high enough, a good reversibility of the ‘doping’ process is observed from increasing to decreasing ‘dopant’ concentrations (Figure 6).

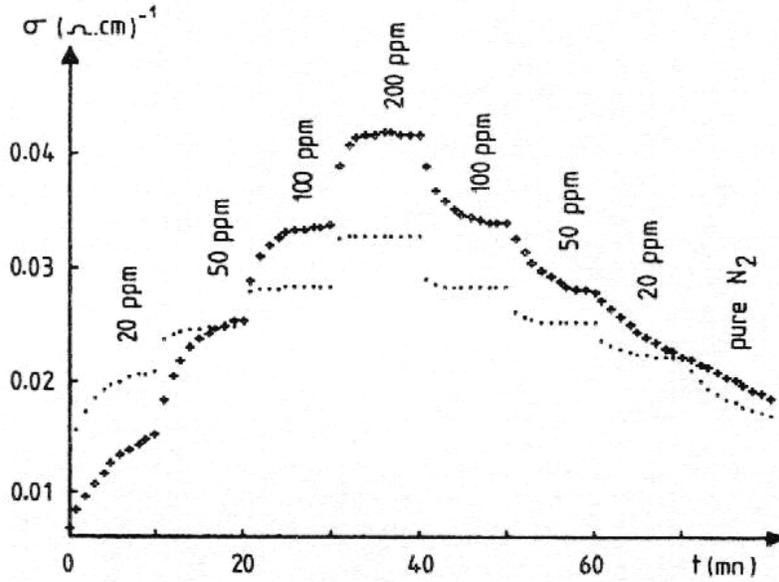


Figure 6. Conductivity vs. time for increasing and decreasing NO₂ concentration steps at T = 120 °C (+) and T = 180 °C (•)

For temperatures ranging from 140 to 180 °C, the response time is short enough for a gas sensor application. Moreover, in this temperature range the stability of the sensor is satisfactory (Fig. 7).

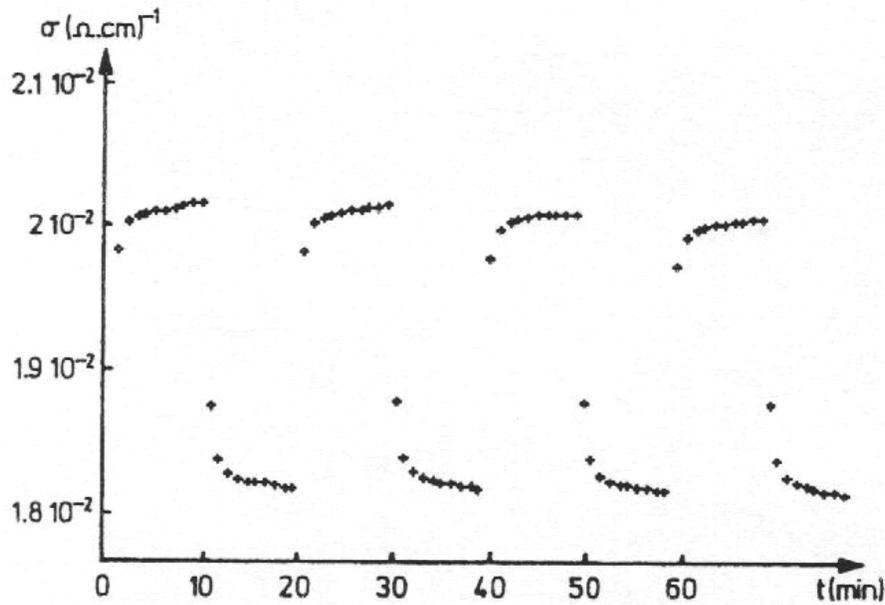


Figure 7. Conductivity vs. time for alternated ‘dopings’ with 200 and 100 ppm NO₂ at 160 °C.

IV. DISCUSSION

The action of an oxidizing gas such as NO_2 can be described by a gas adsorption followed, if the electroaffinity of the gas and the ionization potential of the polymer are convenient, by a charge transfer between the gas and the polymer which produces an increase in its conductivity.

In order to study these phenomena, thin layers of $(\text{AlPcF})_n$ of various thicknesses and deposition rates have been doped at 100 ppm then 50 ppm NO_2 during 2 hours at a constant temperature of 160°C . The results are similar on all samples (Figure 8).

Whatever the layer thickness is, and although the electrodes lie **under** the polymer layer, we note that the conductivity increases as soon as NO_2 is introduced into the cell, thus demonstrating that the layer is spongy and that all the grains are rapidly in contact with the gas.

With the hypothesis that each NO_2 adsorbed molecule participates to the charge transfer and thus to the macroscopic conductivity of the layer, we can apply the chemisorption and diffusion theories to our experimental curve of figure 8.

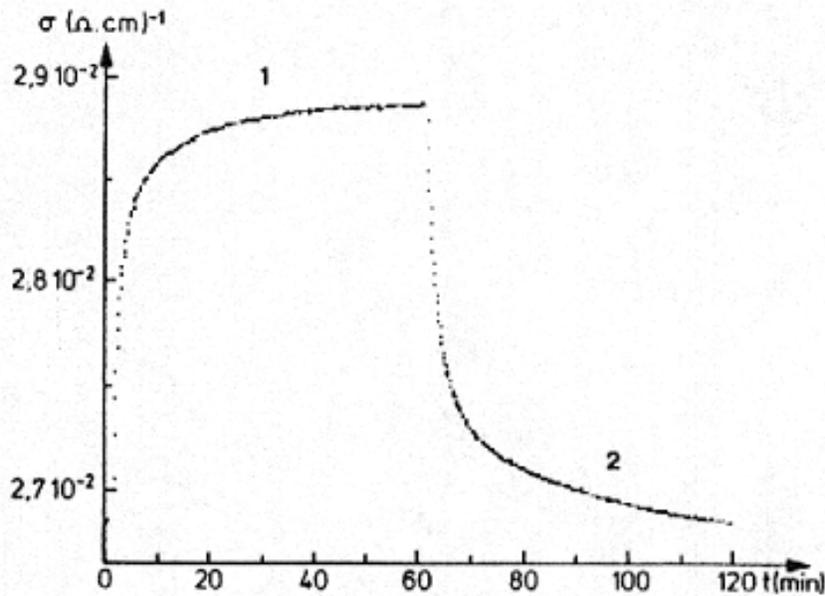


Figure 8. $(\text{AlPcF})_n$ conductivity vs. time for 'doping' by 200 ppm NO_2 (1) and 50 ppm NO_2 (2), at $T = 160^\circ\text{C}$.

This means that during doping, the gas is primarily adsorbed at the surface of the grains, according to an Elovich equation, and then diffuses in their bulk, with an exponential time law.

When the NO₂ concentration is decreased from 100 to 50 ppm, desorption of the gaseous molecules previously adsorbed on the surface proceeds first, followed by the gas diffusion out of the bulk of the grains [18].

V. A DEVOTED APPLICATION : AIR POLLUTION MONITORING

V.1. Context :

In industrialized countries, the growth of production and traffic contribute to the degradation of air quality [19, 20]. In relation with an increasing interest for environmental questions all over the world, the demand of new measurements increases. This demand concerns the multiplication of the data available all over the territories, not only in the big cities as thirty years ago, but more and more in every town and even in the countryside. The species studied by specialists of the air quality control are mainly carbon monoxide (CO), carbon dioxide (CO₂), sulphur dioxide (SO₂), nitrogen monoxide (NO), nitrogen dioxide (NO₂) and ozone (O₃) due to their toxicity for populations and to vegetation impacts. More and more new molecules are analyzed as polyaromatic hydrocarbons such as benzene, toluene, xylene and various solvents. These measurements are achieved also inside buildings even though the concentrations are smaller than outside. Indeed, long-term exposures at low concentrations can lead to the same effects than short-term exposures at upper concentrations [21, 22]. Moreover, specific pollutants, such as ozone produced by copy machines, and solvents issued from domestic uses can cause medical damages. So, since several years, atmospheric pollution has become a problem of public health. Amongst all the gases present in atmosphere, some of them are dangerous in high concentrations and must be monitored. In general, the techniques used to carry out measurements use spectrophotometers whose prices are approximately ten thousand euros. Therefore, one of the main advantages of sensors compared to classical analyzers is surely their price and so the possibility to multiply the number of measurements all over the territories.

V.2. Phthalocyanine Chemiresistor : Gas Sensor Results :

The molecular semiconductor sensor is a thin film of copper phthalocyanine deposited under vacuum (2×10^{-6} mbar), on an alumina substrate fitted with interdigitated Pt electrodes to measure the conductivity of the sensitive layer (Fig. 9). The purity of phthalocyanine is improved by

evaporation under vacuum. The process is the sublimation of the phthalocyanine powder during few minutes before deposition of the sensitive layer, to eliminate impurities. The dimensions of the structure are 5×3 mm, the thickness of the CuPc film is 300 nm and the deposition rate is 2 \AA per second at room temperature. On the other side of the substrate is the same screen-printed Pt resistor as above for heating.

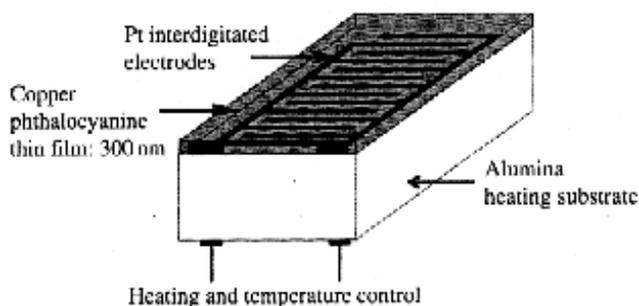


Figure 9. CuPc-base device.

Two sensors are kept at $50 \text{ }^\circ\text{C}$ and submitted to 100 ppb NO_2 then 100 ppb O_3 (Fig.10) [15, 23]. The two polluting species give responses with roughly the same sensitivities: the detection is not selective. Thus, to measure only the conductivity of the phthalocyanine resistor does not allow to discriminate the nature of the polluting gas.

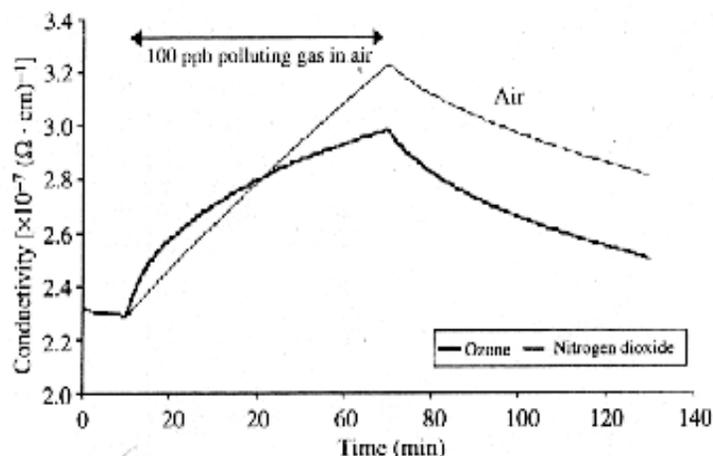


Figure 10. Conductivities of 300 nm CuPc layers at $50 \text{ }^\circ\text{C}$ in synthetic air ($20\% \text{ O}_2 + 80\% \text{ N}_2$) and submitted to 100 ppb NO_2 or O_3 in air.

Figure 11 represents the conductivity variations of a 300 nm-thick film of CuPc heated at $80 \text{ }^\circ\text{C}$ submitted to various concentrations of ozone [24]. The curves show a great variation of relative

conductivity in coherence with the strong sensitivity of phthalocyanine materials in detection of oxidizing gases. But, in all cases, thermodynamic equilibrium is not reached after one hour of exposure and desorption is not satisfactory at 80 °C.

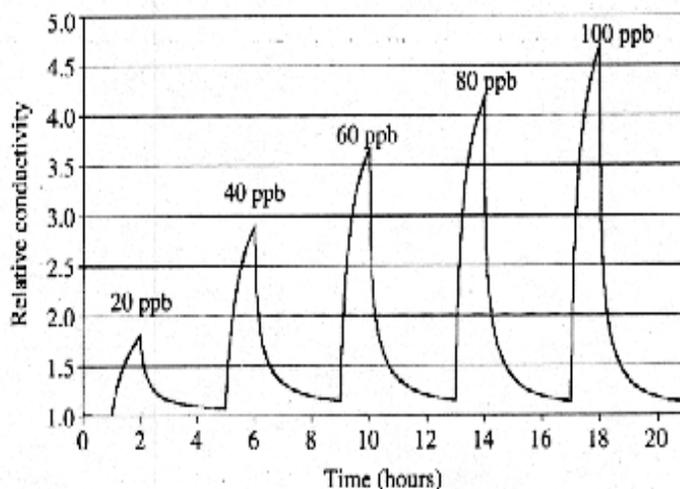


Figure 11. Conductivity variations of a 300 nm-thick CuPc layer heated at 80 °C submitted to 20, 40, 60, 80 and 100 ppb of ozone with desorption under clean air after each exposure.

Moreover, reproducibility is also affected by the slow regeneration of the sensitive layer. The kinetics of reactions may be improved by increasing the operating temperature [25]. This improvement is obtained to the detriment of the sensitivity of the detection. A compromise must be found in the context of the polluting gas detection : in order to enhance the sensitivity and in view of our application field, where very small quantities of gases are present, a low operating temperature was chosen, favouring adsorption process.

VI. CONCLUSION

This research work has proved that (AIPcF)_n could be a sensitive polymer for an NO₂ sensor. Operation in air should be possible because of the slight effect of oxygen on the conductivity, with the assumption that oxygen does not occupy many of the empty spaces in the lattice, which would then prevent the penetration of the NO₂ molecules.

The NO₂ doping kinetics has been successfully interpreted in agreement with the theories of gas adsorption on the surface of the polymer grains and diffusion in their bulk.

The reversibility of charge transfer and gas sorption makes the 'dedoping' of (AIPcF)_n possible.

The response of (AlPcF)_n thin films to NO₂ and O₂ presents some interesting characteristics (reversibility, short response times, sensitivity to the gas concentration, ...) for use of this material as sensitive element of gas sensors.

Moreover, the similar results obtained with the two types of substrates prove the good compatibility of polymeric sensors with microelectronics techniques.

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