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A Neural Based Intelligent Interpretation System of Detected Gases Using PbPc Gas Sensor Array

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Abstract: The voltage/current characteristics and the effect of NO₂ gas on the electrical conductivity of a PbPc gas sensor array is investigated. The gas sensor is manufactured using vacuum deposition of gold electrodes on sapphire substrate with the lead-phthalocyanine vacuum sublimed on the top of the gold electrodes. Two versions of the PbPc gas sensor array are investigated. The tested types differ in the gap sizes between the deposited gold electrodes. The sensors are tested at different temperatures to account for conductivity changes as the molecular adsorption/desorption rate is affected by heat. The obtained results found to be encouraging as the sensors showed stability and sensitivity towards low concentration of applied NO₂ gas.

Key words: Intelligent system, PbPc, gas sensor, hardware, software, neural network

INTRODUCTION

The gases absorbed on the surfaces of the organic materials have a marked effect on the electrical conductivity of these materials; where the electrical conductivity of an organic material that contains transition and heavy central atoms changes by many orders of magnitude when a gas adsorbs on its surface.

Adsorption involves the formation of bonds between the adsorbed gas and the organic material, by transfer of electrical charge. The charge transfer changes the electronic structure of the material; changing its conductivity. Changes in the conductivity are related to the number of gas molecules adsorbed on the surface and hence, to the concentration of the adsorbed species in the surrounding atmosphere. The measurement of changes in electrical conductance due to gas adsorption makes organic materials ideal for the detection of low gas concentration.

The conductivity of an organic material can either be affected at the surface with no bulk interaction, or following the reaction at the surface; carriers can be injected into the bulk causing both surface and bulk conductivities to be affected (Carotta *et al.*, 2001; Hatfield *et al.*, 2000; Gardne *et al.*, 1999a, b).

When a gas molecule chemisorbs on the surface of the organic material, an electron or electrons may be transferred from one to the other, where the direction of

transfer depends on the electro negativity of the gas and the work function of the solid. Also the physisorption of the gas plays an important role in the overall mechanism of gas adsorption and subsequent conductivity changes in the organic material. The adsorption of the gas molecules as ions on the surface removes electrons from the solid and localizes them at the surface, thus generation electron traps in the solid. This result in an increase in the hole concentration and therefore an increase in the conductance as the material will function as a P-type material.

In this study the properties of the PbPc sensor array is confirmed and employed in an intelligent discriminating and controlling system. The system uses the inter-digital geometry together with PbPc film properties to distinguish between types of gases and alert to any increase in the level of these gases above acceptable levels.

Metal-phthalocyanines: They are a group of organic materials known to have several properties that make them attractive as a potential gas sensing materials or gas detectors. They have the following desirable properties:

- They are considered to be good electrical conductors, where the charge carriers are known to be positive holes (Gutierrez-Osuna *et al.*, 2003; Gardner and Iskandarani, 1992).

- Reaction of Phthalocyanines with electron accepting gases should increase its conductivity.
- They are thermally stable to temperatures in excess of 400°C centigrade.
- They can be used for extended periods at elevated temperatures.
- Organic groups can be easily modified and functional groups can be substituted on either ring structure or on the central hydrogen atom in the metal-free Phthalocyanines (H₂Pc) as shown in Fig. 1.

Several of the Metal-Phthalocyanine materials (e.g., commercial materials) contain significant amounts of impurities which can result in irreproducible electrical characteristics, which can be purified using either Gas-Entrainer Sublimation (in nitrogen or oxygen) or by vacuum sublimation (the used technique in present study). The purification process leads to stable and reproducible electrical characteristics. Early studies of Phthalocyanines showed that many are sensitive to the presence of NO₂ with an increase in the sensitivity observed when the Phthalocyanines contains heavier central atoms.

Metal-phthalocyanines organic semiconductors found to undergo conductivity changes upon the adsorption of strongly electrophilic gases such as NO₂, CL₂ and F₂. The magnitude and reversibility of these conductivity variations found to be dependant on the central metal species. Because of their high decomposition temperatures (450°C), phthalocyanines can be vacuum evaporated to produce thin films. The deposition of such films on the surface of a substrate

eliminates some of the complications arising from having to consider both surface and bulk conductivities in the analysis process. The absence of bulk conductivity effect will improve the response and recovery times of the designed sensor array. However, the presence of impurities will affect resistivity, linearity, hysteresis and drift of the electrical characteristics. Also the conduction activation energy and the specific conduction mechanism will be affected.

Lead-phthalocyanines (PbPc): It is the most sensitive and stable Phthalocyanine material. Although, insensitive to a wide range of gases (e.g., weak electrophilic and electrophobic gases and CH₄, CO, CO₂, H₂O, H₂, Hydrocarbons and changes in O₂ pressure) (Fig. 2), PbPc based sensor is very sensitive and potentially useful in detecting strong electrophilic gases particularly to NO₂ or NO_x and will respond to low concentrations of F₂ and less than 1 ppm concentration of CL₂ gases. Thus it could form the basis of a highly sensitive and selective NO₂ or NO_x sensor and it is suitable for detecting these gases at concentrations from 1 ppb to 10 ppm in air and retains discrimination to concentrations above 100 ppm.

Since PbPc has high sensitivity and selectivity to strongly accepting gases such as NO₂, CL₂, F₂ and O₃, discrimination between strongly accepting gases and other gases is achieved by careful choice of operating temperatures. However, the stability and electrical properties of this type of sensors is affected by water vapor, so a heating element is usually fitted to the back of the sensor to eliminate such factor.

It is found (Gardner and Iskandarani, 1992) that PbPc sensor is most sensitive to NO₂ gas and can be operated

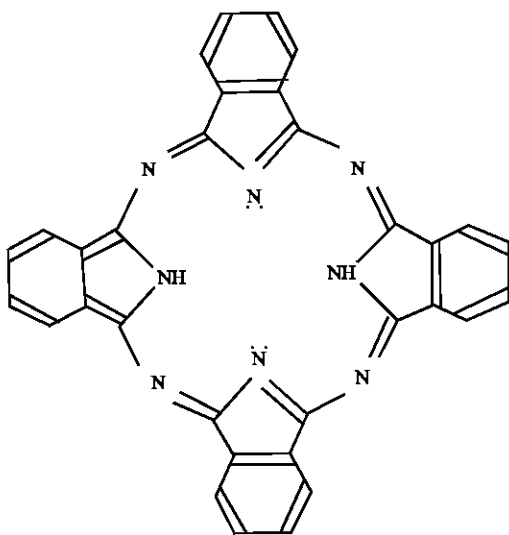


Fig. 1: H₂Pc molecular representation

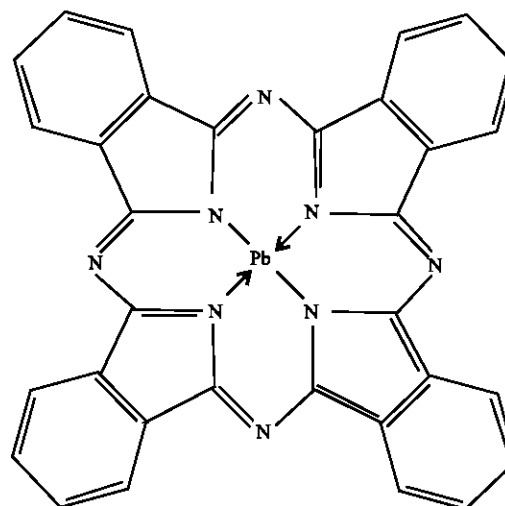


Fig. 2: PbPc molecular representation

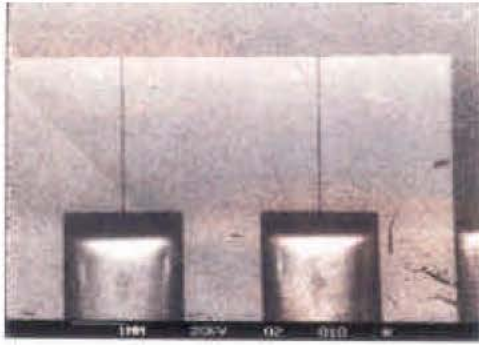


Fig. 3: 10:10:10 gap separation

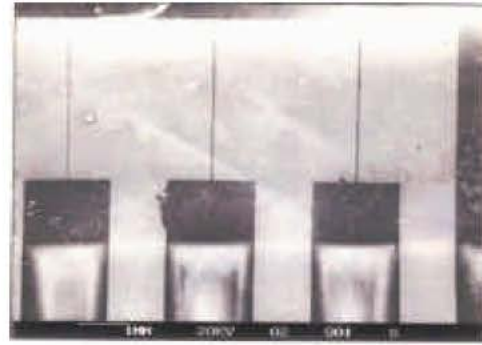


Fig. 4: 510:15 gap separation

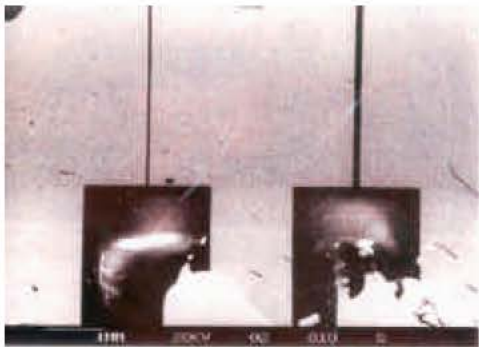


Fig. 5: 10:33 gap separation

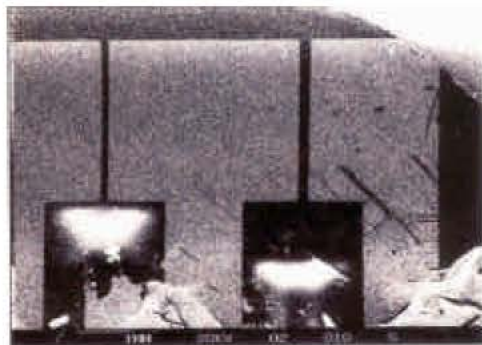


Fig. 6: 33:100 gap separation

in a continuous mode at temperatures above 100°C with its sensitivity and stability decreasing as the temperature approaches 200°C. These temperatures are also a function of PbPc film thickness deposited on the substrate and can be extended when thick films are used.

PbPc sensor design: The sensor is based on a sapphire substrate ($\text{Alpha-Al}_2\text{O}_3$), which usually contains traces of Fe and Ti ions. The substrate has a very high melting point (about 2050°C). It is very hard and quite inert, especially towards acids. The substrate has an area of 12.5, 12.5 mm. Different types of electrode gap separations are produced to study the effect of inter-electrode separation of sensor sensitivity as shown in SEM photographs in Fig. 3-6. The sensor is mounted on a transistor like base, as it comprises three gaps.

Experimental setup: A testing chamber is built with air and temperature controls supplied through a computer controlled unit. Electrical characteristics of the sensor and its response to gases are recorded via specially designed hardware/software system as shown in Fig. 7 (Cole *et al.*, 1999; Hines *et al.*, 1999a,b; Dyer and Gardner, 1997; Gardner *et al.*, 1996).

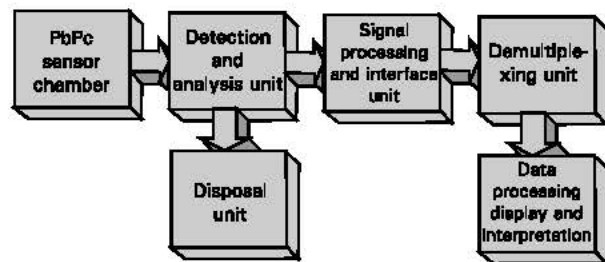


Fig. 7: Testing system

Sensor interface circuit: The obtained signals from the PbPc sensor array is known to have relatively small values, hence, a differential amplifier interface circuit is designed and used to condition the sensor output signal to the remaining part of the signal processing system, which also includes A/D converter and noise filters. The basic amplifying unit is shown in Fig. 8 (Perera *et al.*, 2002; Gardner *et al.*, 2000; Gutierrez-Osuna and Nagle, 1999).

In Fig. 8 each two inter electrodes produce a voltage signal proportional to the gap size and film thickness of the deposited PbPc film. The difference in the voltage of

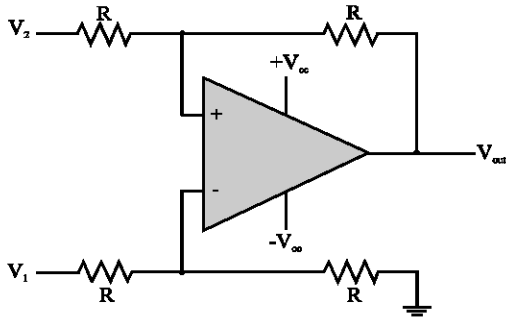


Fig. 8: Differential Amplifier Interface Unit

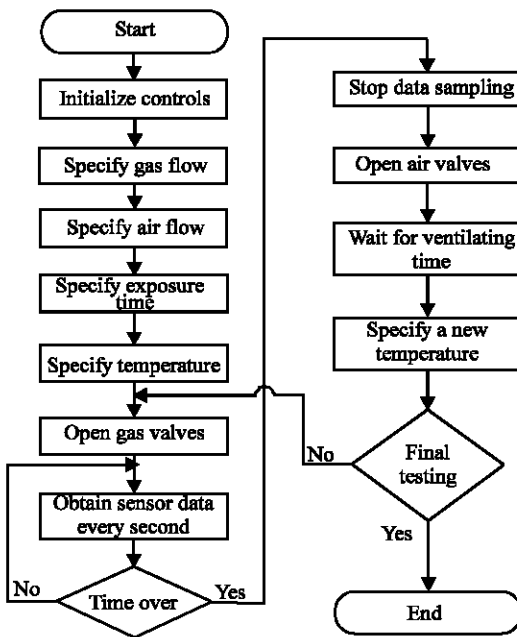


Fig. 9: Interface algorithm

each two electrodes is amplified and processed to the next stage. The amplifying unit acts as an impedance

matcher, so that a correct measure of the detected gas level is acquired with minimal signal loss.

Interfacing algorithm: After digitizing the amplified and cleaned sensor array signals, they are processed to be analyzed using the algorithm shown in Fig. 9.

DISCUSSION AND CONCLUSION

Table 1 shows the testing results of our array sensor, which clearly indicates an increase in the output signal response of the sensor as a function of three main factors:

- Distance between conducting electrodes (Interdigital separation).
- Increase in atmospheric temperature.
- Effect of gas concentration.

These factors can be used to control the behavior of the sensor in terms of the amount and type of adsorbed odors and the rate of desorption. The Table 1 also shows that the increase in output signal current is exponential. The mathematical law governing the response of the sensor is affected by the way the Organic Semi conducting layer is sublimed and its thickness and uniformity.

Overall the obtained characteristics of the tested groups of sensors very much agree with the literature and more proves the response shape of such sensor to be a specific case of power law response, which is a real exponential. Each sensor can be modeled as a group of three sensors grouped together which initiates the need to use pattern recognition and smart classification techniques for complex analysis.

Using initially obtained values of voltage, temperature and inter electrode separation, a neural model is built as shown in Fig. 10 (Gutierrez-Osuna and Gutierrez-Galvez, 2003; Cole *et al.*, 2001; Shin *et al.*, 2000; Gutierrez-Osuna and Powar, 2003).

Table 1: Testing results of array sensors

Voltage (mV)	Current (pA) -110°C			Current (pA) -130°C			Current (pA) -150°C		
	Gap 5	Gap 10	Gap 15	Gap 5	Gap 10	Gap 15	Gap 5	Gap 10	Gap 15
50	3.025	3.147	2.7950	2.708	3.3980	4.4320	3.8340	3.8960	9.4120
100	3.265	3.540	3.6100	3.305	3.8860	6.4130	4.7840	4.5450	17.796
150	3.475	3.895	4.3440	3.896	4.3950	8.3200	5.7470	5.2680	32.820
200	3.602	4.266	4.8260	4.420	4.8800	10.375	6.7050	6.0420	41.730
250	3.791	4.650	5.5060	4.910	5.4400	13.095	7.9160	6.7940	45.570
300	3.990	4.970	6.3040	5.395	5.9700	16.785	8.8880	7.5960	46.700
350	4.160	5.265	7.0590	5.999	6.4600	26.200	10.013	10.395	46.730
400	4.301	5.550	7.6650	7.194	6.9850	34.690	11.118	11.294	46.820
450	4.480	5.760	8.0670	7.265	7.6100	37.920	11.806	12.185	46.820
500	4.625	6.065	8.1620	7.746	8.2700	41.460	13.045	13.323	46.820
550	4.789	6.390	8.8530	8.323	8.8980	44.420	14.196	14.396	46.820
600	4.932	6.699	9.6180	8.815	9.4210	45.890	15.296	15.595	46.820
650	5.150	6.979	10.935	9.398	10.221	46.350	16.650	16.946	46.820

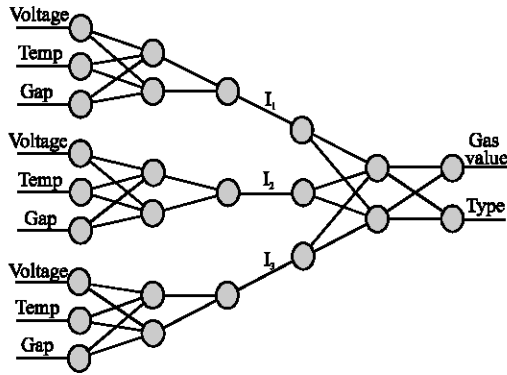


Fig. 10: Neural Model for sensor array

Table 2: Predicted values for the 5:10:15 sensor array

Voltage	I ₁	I ₂	I ₃
50	2.88	3.00	2.65
100	3.10	3.36	3.43
150	3.30	3.70	4.13
200	3.42	4.05	4.58
250	3.60	4.40	5.23
300	3.79	4.72	6.00
350	3.95	5.00	6.70
400	4.10	5.27	7.28
450	4.25	5.47	7.66
500	4.39	5.76	7.71
550	4.55	6.07	8.41
600	4.68	6.36	9.13
650	4.89	6.63	10.38

This model associates the three mentioned important parameters, which implicitly determined the sensor array currents that enable the system to determine and predict level of gas concentration and type of detected gas. The model operates using back propagation principles such that the sensor array system can be used as both gas type discriminator and gas level controller. Both applications are very important in terms of distinguishing between types of gases (e.g., Normal or hazardous) and if the level of gas exceeds a preset safe limit will operate as a controlling system indicator.

The constructed neural model is tested to after being trained using Back propagation algorithm. Table 2 shows the predicted results for the 5:10:15 sensor array at 110°C. The obtained neural results are evidently very close to the experimental ones. This is partly due to proper pruning of the neural network and the use of several hidden layers (Gardner *et al.*, 1999a, b; Llobet *et al.*, 1999; Hines *et al.*, 1999a,b; Gardner *et al.*, 1998; Vlachos *et al.*, 1997; Vlachos and Avaritsiotis, 1996).

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