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Published version

HAMID, Amani, HOLLOWAY, Alan, HASSAN, Aseel and NABOK, Aleksey (2016). Investigation and analysis of zinc phthalocyanine films for resonant gas sensor applications. Procedia engineering, 168, 259-263.

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ScienceDirect

Procedia Engineering 168 (2016) 259 – 263

Procedia Engineering

www.elsevier.com/locate/procedia

30th Eurosensors Conference, EUROSENSORS 2016

Investigation and Analysis of Zinc Phthalocyanine films for Resonant Gas Sensor Applications

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Abstract

Thin films of Zinc Phthalocyanine (ZnPc) with a range of different substitutes have been investigated as chemical active layers for sensing selected organic vapour such as (Ethanol, Toluene) by a standard Quartz Crystal Resonator (QCR) based sensor with fundamental resonance 10MHz. Adsorption of vapour onto the films surface has been realized by monitoring resonance spectra. An equivalent circuit (BVD circuit) has been used to extract parameters related to film viscosity and thickness by fitting experimental admittance spectra of QCR around resonance frequency. Moreover, film properties and characterization was obtained from QCR measurements in conjunction with suitable data analysis. Validation of film characteristics has been determined using complementary methods such as Ellipsometry, UV- Visible absorption Spectrophotometer and AFM.

Keywords: Zinc Phthalocyanine, Quartz Crystal Resonator (QCR)

1. Introduction

Phthalocyanine films have become an increasingly important field of study, with several research groups investigating phthalocyanines in sensor applications utilizing a range of techniques and transduction mechanisms;

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doi:10.1016/j.proeng.2016.11.183

investigating areas such as chemical interaction with gases and the performance of sensing devices. This can be attributed to the properties of the resultant sensitive absorption layers such as high stability, sensitivity, selectivity and the ease of which they be applied as a thin films through traditional coating methods[1,2,3]. Additionally, variations in sensing/detection properties can be realised by the addition of different substituent in the phthalocyanine film [4,5].

In this work, the impedance analysis approach was performed to explore vapour adsorption of organic solvents by several ZnPc substituents. The technique allows additional information about film parameters to be extracted as compared standard oscillator measurements and presents an insight into changes appearing in the film as a result of vapour adsorption [6,7].

2. Experimental

2.1. Sensitive materials

Zinc phthalocyanines with four different substituents were studied and characterized for their gas sensing performance. Table 1 shows the specific materials used; an identification code has been assigned to each substituent pattern. All phthalocyanines (Pcs) used in this work were obtained from Sigma-Aldrich.

Table 1. Materials and their codes and substituting pattern.

Chemical name	Substituting pattern	Code	Empirical formula (Hill Notation)
Zinc2,3,9,10,16,17,23,24octakis(octyloxy)-29H,31H phthalocyanine	Zn-oct-oct-Pc	a	$C_{96}H_{144}N_8O_8Z$
Zinc 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro 29H,31H-phthalocyanine	Zn-hex-Pc	b	$C_{32}F_{16}N_8Zn$
Zinc 1,4,8,11,15,18,22,25-octabutoxy- 29H,31H-phthalocyanine	Zn-oct-Pc	c	$C_{64}H_{80}N_8O_8Zn$
Zinc 2,9,16,23-tetra-tert-butyl-29H,31H-phthalocyanine	Zn-tp-tb-Pc	d	$C_{48}H_{48}N_8Zn$

2.2. QCR transducer & Sensor Preparation

The QCR transducers used in this work were 10MHz fundamental resonant frequency AT-Cut quartz crystals. Spin coating was used for deposition of the ZnPcs on the transducers. Solution of sensitive material was prepared by dissolving the ZnPc in analytical grade chloroform at a concentration of 10mg/ml at room temperature. A micropipette was then used to drop a known amount of solution onto the rotating (2000rpm) substrate surface; the solvent subsequently evaporates leaving the desired film. No further chemical or physical treatment of sample was performed after deposition. Impedance/Admittance measurements at a range of frequencies around crystal resonance were then taken and resultant spectra fitted to the BVD equivalent circuit. Two common organic solvent were used as test analytes: (Ethanol and Toluene). Concentrations in the range of Lower to Higher Explosion Limit (LEL-HEL), where used for each analyte.

2.3. Vapour exposure

A typical measurement protocol is as follows: The sample measurements were undertaken in a Teflon chamber with an internal volume of approximately 0.0636 m^3 and the inlet pipe was located on the top of the chamber. Measurements were taken using a Keysight E4990A impedance analyser controlled via PC running LabVIEW software to continuously record the spectra during exposure. Specific amounts of liquid test analyte relating to the required concentration are deposited into the chamber through a micro syringe and allowed to evaporate. The chamber was flushed with air after every exposure in order to test if full recovery of the QCR sensor response is observed. The Admittance (reciprocal of impedance) spectra obtained by measurement were then fitted to the BVD equivalent circuit by using LabVIEW program and parameters (Δf and ΔR related to L_{load} and R_{load}) extracted [6].

3. Result and discussion

Definite shifts in the resonance peak of QCR sensors coated with (Zinc-octabutoxy- phthalocyanine) are observed after the coating processes, as illustrated in Fig. (1). Also the change in admittance magnitude in addition to frequency can be interpreted as a viscous film response (film damping and mass loading). Notable differences were obtained in the calculation of film thickness directly from the frequency shift using the Sauerbrey equation as compared to film thickness obtained from the Ellipsometry and AFM based measurements. This can be attributed to the effects of the viscoelastic film.

The change in both frequency of QCRs and the maximum admittance values after coating process with ZnPc films are listed in Table 2.

Table 2. Materials and their codes with corresponding frequency and admittance change after coating process.

Code	Substitution pattern	Frequency change Δf (Hz)	Maximum admittance change ΔG (S)
a	Zn-oct-oct-Pc	7656	0.010294
b	Zn-hex-Pc	16878	0.06791
c	Zn-oct-Pc	5312	0.005018
d	Zn-tp-tb-Pc	4313	0.039902

Different levels of sensitivity to the target vapours have been obtained by the selected (ZnPc) films. For the (Zinc-octabutoxy- phthalocyanine) film there is an approximately linear relationship of sensor responses for both Ethanol and Toluene. Plots of the sensitivity with concentration in absolute units of parts per million and relative vapour pressure are represented in Fig. 2 and 3 respectively for films a, b, c and d. The response plots and kinetic characteristics observed during exposure (fast and reversible) demonstrate good potential for the use of ZnPcs coated QCR sensors.

Considerable changes in magnitude and frequency which indicate mass loading and film damping are also obtained on vapour exposure. As Figure 4 depicts there are changes in the films viscoelastic properties for higher concentrations of Ethanol and Toluene which can be observed from a negative frequency shift ($\Delta \boldsymbol{f}$) and changes in magnitude (related to ΔR of the BVD equivalent circuit). Fig. 5 shows the relation between $\Delta \boldsymbol{f}$ and ΔR of Zn-oct-oct-Pc, Zn-hex-Pc, Zn-oct-Pc and Zn-tp-tb-Pc compound on vapour exposure. Via the use of a specific phthalocyanine substituent a unique correlation in this ratio could be possible, enabling enhanced sensor selectivity and discrimination particularly in the higher concentration range**.**

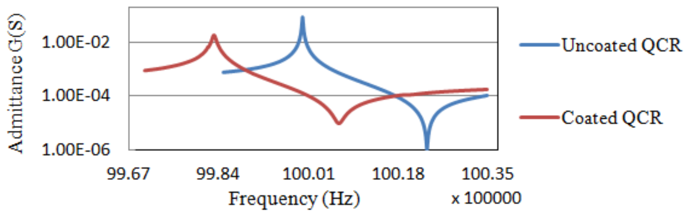

Fig. 1. Admittance magnitude for QCM before and after coating with Zinc-octabutoxy- phthalocyanine film.

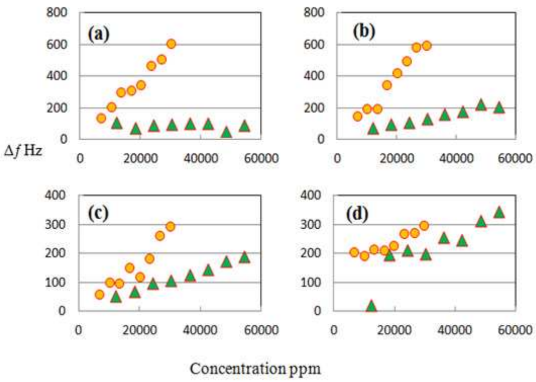

Fig.2. Δf against vapour concentration in ppm relative to air.

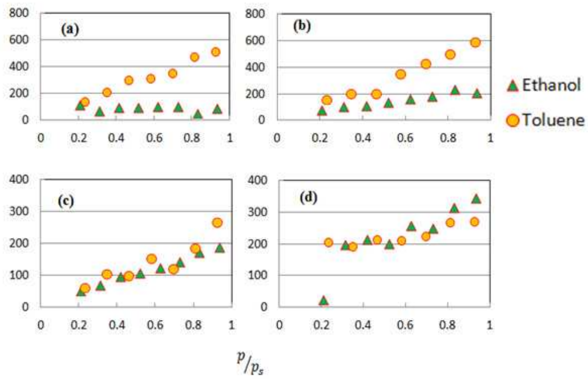

Fig.3. Δf against vapour concentration relative to saturated vapour pressure.

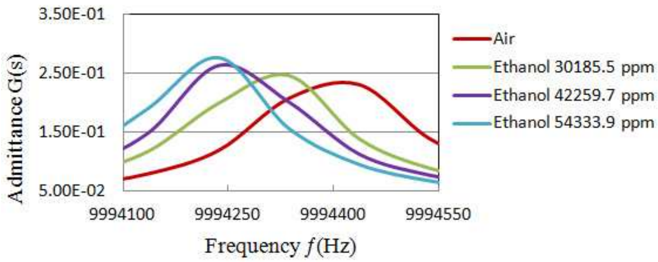

Fig.4. Admittance magnitude against frequency for higher concentrations of Ethanol vapours of Zinc-octabutoxy- phthalocyanine film.

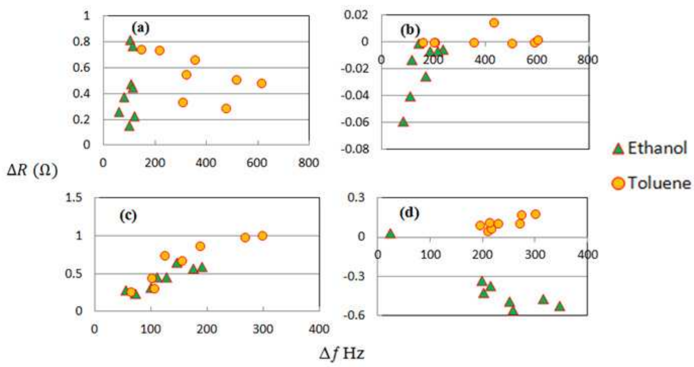

Fig.5. *ΔR* against Δf of (a, b, c and d) films.

4. Conclusion

This paper proposes and describes the usage of substituted Zinc phthalocyanines in QCR gas sensing of organic thin film in gas environments. Four different sensitive materials were successfully tested and studied in their sensing performance using two different common organic analytes (Ethanol, Toluene), and were found to exhibit good sensitivity. In addition to the result of sensitivity, short response time and full recovery are observed. Changes in both Δf and ΔR indicating a viscoelastic contribution to the sensor response potentially give the basis for discrimination between different organic vapour. The ZnPcs tested shows a promising performance for future use in sensor applications, further work is in progress to fully understand the film interaction and changes in its mechanical properties.

Acknowledgements

This work was supported by University of Tripoli and Sheffield Hallam University.

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