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REVIEW

Phthalocyanines as Sensitive Materials for Chemical Sensors

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This paper provides a review of phthalocyanines suitable for the development of chemical sensors. Phthalocyanines may be utilized for different types of chemical sensors, including in particular electronic conductance sensors [such as semiconductive, field-effect transistor (FET), solid-state ionic and capacitance sensors], mass-sensitive sensors utilizing a quartz crystal microbalance (QCM) and surface acoustic-wave (SAW) sensors, and optical sensors. The phthalocyanines used are discussed in terms of their physical and chemical properties, as well as their sensitivity, selectivity and reversibility towards the detection of NO_2 and organic solvent vapours. The interaction mechanism between phthalocyanine films and analyte molecules is also discussed.

1 INTRODUCTION

Phthalocyanines (Pcs) are organic compounds able to act as chemically sensitive films because of the various physical effects induced in them by interaction with a large number of gases. Specifically, they are used as thin-film semiconducting gas sensors for the detection of halogens such as chlorine (Cl_2) and nitrogen dioxide (NO_2) as well as organic vapours.[1–5] The properties of phthalocyanines, particularly their ionization potentials, can be varied by metal-ion insertion and by the attachment of additional atoms or groups that enhance or diminish the ionization potential by virtue of their position on the electronegativity scale. The variation of the substituents in the side chain and the ligand or μ-bridge in their polymers can cause different detection properties for environmentally relevant gases. This can allow production of carefully designed and optimized thin films having different degrees of sensitivity, selectivity and stability ('sss'). In addition, such films have high chemical and thermal stability towards many environmental conditions. They can easily be produced as films through coating methods such as sublimation, spraying, and spin and smearing-coating.

The interactions between the Pc films and the gases may be classified in terms of irreversible chemical affinity, reversible (usually charge-transfer) chemical reaction or bulk sorption. These interactions result in detectable changes in physical properties of the films which include conductivity,[1–4, 6, 7] mass,[4, 5, 11] and optical properties.[8–10]

In this review, differnt types of nitrogen oxide, NO_x and organic solvent vapor sensors based on Pc films are discussed according to their film structures and their electric properties. The gas sensors to be discussed include electronic conductance sensors such as semiconductive, field-effect transistor (FET) and solid-state ionic sensors, capacitance sensors, mass-sensitive sensors utilizing a quartz crystal microbalance (QCM) and surface acoustic-wave (SAW) sensors and optical sensors.

2 ELECTRONIC CONDUCTANCE CHEMICAL SENSORS

Electronic conductance chemical sensors are chemically sensitive solid-state devices whose operation is based on changes in electrical

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properties. The changes may be in the electronic conductivity or mixed electronic and ionic conductivity (conductance sensors), and/or in the capacitance (capacitance sensors). Other terminologies commonly used for these sensors include homogeneous and heterogeneous semiconductance, and Schottky diode and dielectric sensors.[1,3] Semiconductive, capacitance, field-effect transistor (FET) and solid-state ionic sensors which utilize phthalocyanines and its derivatives as chemical interfaces are discussed below.

2.1 Semiconductive sensors

It is well-known that p-type organic semiconductor Pc films exhibit very high sensitivity to electrophilic gases such as NO_2 and Cl_2.[12,13] This high sensitivity to electrophilic gases is due to an interaction with the Pc thin films which results in a large change in the electrical conductivity of the film. The gas sensing is realized through a charge-transfer interaction in which the gas molecule to be sensed acts as a planar π-electron acceptor forming a redox couple. The positive charge produced is then delocalized over the Pc ring, causing an increase in the conductivity. Several reported observations and results which give a useful insight into the mechanism by which the interactions promote a conductivity change have been summarized.[4,14] A detailed description of the Pc properties, of the gas adsorption in Pc films and their effects on electrical properties has also been given.[15] The degree of interaction of the gas, hence the changes in electrical properties depend on the sublimed films of Pc being single-crystalline films, polycrystalline or amorphous films.

Single-crystalline sublimed films

Since Kaufhold and Hauffe[16] first investigated the effects of oxygen (O_2), nitric oxide (NO), NO_2 and ammonia (NH_3) on sublimed thin films of metal-free (H_2Pc) and metal phthalocyanines (MPcs, M = Fe, Co, Cu and Zn) and showed that NO_x interaction resulted in a large increase of conductivity, sublimed films of the phthalocyanine derivatives have received wide attention for the detection of NO_x and halogen gases.[1,3,13]

The properties of single-crystalline thin films of H_2Pc and MPcs (M = Mn, Co, Ni, Cu, Zn and Pb) were quantitatively studied by van Ewyk.[17] Surface conductivity of the Pc films was found to increase by a factor of up to 10^8 upon exposure of NO_2 and dinitrogen tetroxide (N_2O_4). At low concentrations of NO_2 and N_2O_4, the magnitude of the increase was found to follow a Freudlich adsorption isotherm, and the saturation conductivity at high pressure is similar for all Pcs investigated.[17] This interaction mechanism was interpreted as the formation of a charge-transfer complex between the Pc donor and NO_2 acceptor, and the charge carriers are holes produced in the Pc matrix.[17] It was also pointed out that the nature of the acceptor is important for the conductivity-enhancing effect. NO_2 is a π-electron acceptor, and the accepted electron would be delocalized over the planar NO_2 and N_2O_4 molecules. Since the hole is also delocalized over the Pc structure, the coulombic force between the opposite charges is weakened and charge-carrier movement is facilitated. In addition, the results showed that reversibility of the absorption or adsorption upon heating in vacuum depends on the metal. Reversibility of gas absorption or adsorption for H_2Pc and MPcs (M = Ni, Cu, Zn) is greater than that for CoPc and MnPc. The same is true for MnPc compared with PbPc.

The response time of the single-crystal Pc films is related to the cycling times of the layers exposed to NO_2.[18] The response of single-crystalline thin PbPc films during the first cycles of exposure to NO_2 is initially very slow. However, the second and later cycles were found to produce a faster response and therefore result in a larger increase of conductivity. Clearly, this cannot be explained in terms of surface crystallization, since further structural change will not occur at the temperature of the experiment (150 °C). Note that the condition (temperature) of crystal growth is about 410 °C. However, traces of adsorbed NO_2 will catalyse the adsorption of subsequent NO_2 molecules.

The effects of NO_2 on photoconductivity of single-crystalline layers of ZnPc and PbPc have also been reported.[8] Such effects were found to be more sensitive at low concentrations of NO_2 than semiconductivity effects. However, reversibility is much more difficult to achieve than for the same gases on semiconductivity. As a result, the use of photoconductivity in gas-sensing devices is limited.

Polycrystalline or amorphous sublimed films

It has been observed that the conductivity response of some sublimed thin Pc films to NO_2

appears to be somewhat different from that of single-crystalline Pc films because those films may have an amorphous or polycrystalline character. These defects and disorders affect gas adsorption sites as well as charge-carrier transport. Simple annealing of a sublimed film in the α-crystalline form to the β-crystalline form changes the film's electrical conduction and gas response characteristics.[19] Furthermore, the surface structure of the sublimed films, varied by control of substrate temperature, can be optimized for response to vapours.[20, 21]

The conductivity of a variety of sublimed Pc films is influenced by NO_2, and different Pcs display different conductivity dependence upon the concentration during NO_2 exposure.[13, 16, 18, 22] The responses of several different MPcs exposed to different NO_2 concentrations at 170 °C are shown in Fig. 1. It is seen that thin films of H_2Pc and several MPcs are sensitive to NO_2, whereas PbPc and ZnPc layers combine the higher sensitivity with higher conductance in air than the other transition-metal Pcs.[12, 13] Although H_2Pc films show a similar sensitivity to NO_2 changes, they have a lower conductance. Thus, measurements at low NO_2 concentations are more difficult. In addition, MgPc was found to be very insensitive to NO_2.

The differences in reversibility between polycrystalline or amorphous and single-crystal films are caused by the differences in the temperature of the processes and in the behaviour between thin polycrystalline and single-crystal films of Pcs. Sadaoka *et al.*[23] indicated that the temperature-dependent conductance values for the films with single-crystal whiskers can be formally expressed by the Meyer–Neldel rule with the pre-exponential factor depending on the activation energy. However, the overall enhancement of conductance caused by NO_2 exposure was considerably lower than that for polycrystalline thin films. Ewyk *et al.*[17] explained that the partial reversibility may be due to the bulk effects being irreversible or very slowly reversible while the surface effects are reversible. Archer *et al.*[19] indicated that no bulk gas effect occurred for single-cystal Pc films in their experiments, surface currents were eliminated by the use of an earthed (grounded) guard-ring.

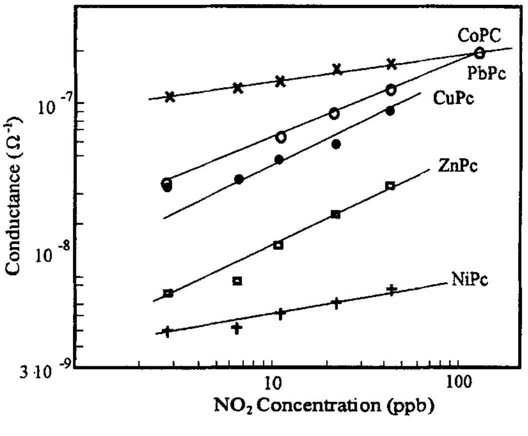

Figure 1 The variation of conductance with NO_2 concentration for some metal phthalocyanines at 170 °C. (Reprinted from *Sensors & Actuators* **9**, T. A. Jones and B. Bott, p. 27 (1986), with kind permission from Elsevier Science S.A., Lausanne, Switzerland.)

As observed in single-crystal layers, fresh sublimed polycrystalline films show that the response to NO_2 is initially very slow. This is understood by the fact that Pc films maintained in NO_2-free air for long periods at elevated temperatures show a slower response to NO_2. Moreover, heat pretreatment at temperatures above the operating temperature caused a gradual increase in conductance, inducing growth of microcrystals without any distinct phase transition, and slightly prolonging the response time.[24, 25]

Sublimed films of electroactive polymers like poly/fluoroaluminium phthalocyanine) $[(AlPcF)_n]$ were also used for the detection of oxidizing gases.[26] The results showed that $(AlPcF)_n$ is a good candidate as a sensitive material for NO_2 gas sensors, since it is characterized by good reversibility, selectivity, sensitivity, stability and response time at high temperature.

Although many sensors coated with sublimed Pc layers have been reported, there exist only few practical devices. For example, Szczurk and Lorenz[27] proposed a practical gas sensor based on a CuPc layer for the detection of high concentrations of NO_2 in air. They also proposed a method for measuring NO_2 concentations in air according to which a complete release of NO_2 from the Pc film after exposure to NO_2 was not necessary and the regeneration process was discontinued after the strength of the electric current had reached a fixed value. In addition, Hamm *et al.*[28] also reported application of a PbPc-coated sensor in environmental control and monitoring and Gentry and Walsh[29] reported that PbPc films can be used as detectors for chlorinated hydrocarbons by Cl_2 sensing from the decomposition of chlorinated hydrocarbons.

Langmuir–Blodgett (LB) phthalocyanine films
Because the thickness and reproducibility of sublimed layers is not easily controlled, other coating deposition techniques, such as the Langmuir–Blodgett (LB) technique, have been developed for Pc films.[30] This technique is very compatible with microelectronic technology and offers excellent control over film thickness and reproducibility. Like their single-crystalline and polycrystalline or amorphous Pc film counterparts, LB Pc films interact strongly with powerful electron acceptors such as NO_x, Cl_2, bromine (Br_2) and iodine (I_2).[30, 31] In fact, the problem with all ligand gas sensors of this type lie not with their sensitivity but their selectivity, for Pc molecules bind several gases.

The first chemiresistor gas sensor utilizing an LB film of Pc was described by Baker *et al.*[31] CuPc, which has been incorporated into LB films consisting of eight LB monolayers, is sensitive to NO_2. The results have indicated that asymmetrically substituted trismethylene isopropylamine Pc LB films exposed to NO_2 showed greatly enhanced response and recovery times compared with LB films of unsubstituted Pc, and that NO_2 interaction is also weaker with peripherally substituted Pc in LB films. Crouch *et al.*[32] reported that LB films of asymmetrically substituted Pc], 4 - bis(4 - hydroxybutyl) - 8, 11, 15,18,22,25-hexahexyl Pc was selective to NO_2. However, the results showed low response to Cl_2 and carbon monoxide (CO) and no effects for sensor response under 0–65% relative humidity. A similar study was reported by Woltjen *et al.*,[33] who studied the effect of ammonia and NO_2 on copper tetracumylphenoxy Pc. Tredgold *et al.*[34] have reported conductivity changes in complexes of mesoporphyrin IX and tetra-arylporphyrin upon exposure to NO_2, H_2S and CO. The conductivity changed by several orders of magitude but long response times were observed, probably due to defects within the 25-monolayers-thick film. In addition, gas-sensing properties of Pc $[(C_6H_{13})_3SiOSiPcGePcOH]$ LB film to halogen gases have been investigated.[35, 36]

It is known that acceptor gases produce a partial oxidation of the tetracyanoquinodimethane (TCNQ) charge-transfer salt to $TCNQ^0$, with a corresponding increase in conductivity.[8, 30] Henrjon *et al.*[37] have also found such effects in LB films of this compound and have shown that they are completely reversible when the device is exposed to ammonia. In addition, LB films of porphyrins have been widely investigated as gas sensor materials for electrophilic molecules.[34]

LB films, however, are expected to be quite fragile and the sensitivity reported is rather low compared with that of sublimed films. Some sublimed Pc films are very sensitive. However, because these Pc molecules are insoluble, they cannot be applied as LB films. These shortcomings limit the application of LB technique in NO_x sensors.

Another type of Pc film obtained by smearing-coating for NO_2 detection was reported.[4, 11] Sensitive films using smearing-coating can be easily produced. However, homogeneous films are difficult to achieve. This nonhomogeneity may influence the response and recovery time of sensors exposed to NO_2 at room temperature.

2.1.1 Interaction mechanism

Two stages of conductivity changes have been reported for sublimed Pc films: these consist of an initial fast change, followed by a slow drift to a steady value when the layers were exposed to gases.[19, 27, 38–40] It was suggested that the fast initial process is due to the surface adsorption of gas molecules into the film.[27, 39] An alternative explanation was given by Archer *et al.*,[19] who proposed a heterogeneous surface site model in which the fast inital change is due to NO_2 adsorption on easily accessible adsorption sites from which oxygen is easily displaced. On the other hand, the slower change is caused by the replacement of O_2 by NO_2 molecules on strong adsorption sites.

For LB films exposed to gases, a linear dependence of conductance on film thickness is obtained, which suggests that the conduction process is primarily a bulk phenomenon rather than a surface effect.[33, 41, 42] In their experimental results, Wang *et al.* also obtained two stages of conductance change in PcLB films and indicated that the conductivity change of the PcLB film arises from the adsorption of the gas molecules on the film surface and subsequent diffusion into the film.[36] Since the sensor measurement electrodes are only in contact with the bottom face of the sensing film, the permeation of the gas into the bulk of the LB film appears to be necessary for maximum response. On the basis of the experimental results, a theoretical model for gas sensing of the LB film was proposed, which considers gas adsorption and desorption on the film surface, and gas diffusion through the film. This model fits the experimental results very well.

Recently, Passard *et al.*[43] proposed a new theoretical model for the interaction between gas and Pc film. They suggested that the oxidation of a Pc by a gas involves processes that lead to the creation of mobile charge carriers and enhancement of the conductivity as follows:

$$\mathrm{Gas+Pc} \overset{\text{physisorption, diffusion,}}{\underset{}{\overset{\text{displacement of species}}{\rightleftharpoons}}} \mathrm{G}$$

$$\mathrm{+Pc} \underset{E_{\mathrm{CT}}}{\overset{\text{charge transfer}}{\rightleftharpoons}}$$

$$\mathrm{G^-Pc^+} \underset{E_{\mathrm{D}}}{\overset{\text{delocalization}}{\rightleftharpoons}} \mathrm{G^-Pc+hole}$$

where G is the molecule of the gas which interacts with the Pc cycles of the film, G^- the ionized gas molecule, E_{CT} the energy of charge transfer (CT) between the two species, and E_D the energy required to free the charge, i.e. to create a mobile hole. From this model, it can be shown that conductivity σ is proportional to $c^{n/2}$ at constant temperature (c is the oxidizing gas concentration and n a constant, $0<n<1$). The relative sensitivity, s, of the Pc is then equal to $n/2$, i.e. the conductivity σ observed in their experimental results is proportional to $c^s(\sigma \propto c^s)$. If Pcs are used as gas detectors, sensitivity to gas concentation variations is not necessary; only a large increase in σ in the presence of a minimum concentation of the gas is required. This is the case for $(AlPcF)_n$ and Cl_2. For gas-sensing applications, high sensitivity of Pc may be necessary. However, in some cases, high sensitivity could be obtained to the detriment of other sensor characteristics. For example, the sensitivity of $(AlPcF)_n$ film exposed to NO_2 is higher at lower temperatues but the response and recovery time are found to vary in the opposite direction.[26, 39, 43, 44] Therefore, operating conditions for the sensor will have to be chosen as a function of the specific applications.

2.1.2 Sensor response

Since conductive sensors based on Pc films have been mainly studied for NO_2 detection, only NO_2 sensors are discussed below. The sensitivity ranges of some Pc-coated sensors for corresponding NO_2 concentration ranges are summarized in Table 1. Here, the sensitivity range is defined as the NO_x concentration range from which useful detector signals may be obtained.

Most of the experiments were performed at elevated temperatures to optimize sensitivity and reduce response times. However, some Pc films have even greater sensitivity at room temperature. The reason for the greater sensitivity to NO_2 at room temperature could be explained by examining the crystal structure of the films.[47, 51, 52] If the substrate temperature is higher during deposition, as reported by Temofonte and Schoch,[9, 47] the stacking axis is parallel to the substrate surface (see Fig. 2). Schramm *et al.*[53] reported that the conductivity in iodine-doped MPc is approximately 100 times higher parallel to the stacking direction than perpendicular to the stacking direction. Therefore, when measuring the sheet resistance of a film, the stacking axes which are parallel to the substrate will produce a much more sensitive NO_2 detector. However, when measuring across the stacking axes, which occurs in films deposited on cooled substrates, sensitivity is lower.

The unique electrical properties of these Pc films also depend on the film morphology associated with the specific deposition approach.[47] Pizzini *et al.*[38] clearly described the influence of the structure and morphology on the sensitivity to NO_x of ZnPc thin-film resistivity sensors. The results have shown that the response times and the sensitivity are strongly dependent on the film structure and morphology, and that the largest sensitivities are not associated with the shortest response time. Sadaoka *et al.*[54, 55] found that the activation energy for conductance is, however, not influenced by the crystal form, and hence the differences in the conductance change for different crystal forms may be caused by the difference of the conductive path.

The reversibility of a sensor depends on the strength of the interaction between the gas and the films. NO_2 is strongly absorbed by Pc films. Elevated temperatures (150–170 °C) are required for desorption,[12, 13, 20] i.e. response and recovery are very dependent upon temperature and film thickness. For NO_2 detection, an increase in temperature from 120 to 170 °C is reported to reduce the 90% response time from 10 to 1.5 min,[12] and a reduction in film thickness from 2.5×10^{-7} m to 3.0×10^{-8} m is reported to reduce the response time by about a factor of 4.[45]

The response time is also dependent on NO_2 concentration and temperature. Temofonte and Schoch[47] reported that the 90% response rise time of the sensors based on films of PbPc at room temperature is about 90 s at a concentration of 25 ppb NO_2. At the same concentration, the NiPc-coated sensors gave a rise time of less than 60 s, whereas Botte and Jones[13] reported a 90% rise time of about 90 s for the films measured at 170 °C on exposure to 50 ppb NO_2. At concentrations of 1.2 ppm, the behavior of PbPc-coated sensors at room temperature[47] is similar to that of thin-film PbPc-coated sensors exposed to 4 ppm NO_2 at 155 °C as reported by Wright *et al.*[15] At the highest concentration (60 ppm), there was an initial fast rise time (<60 s) and then a slower rise time to equilibrium.[47] Baker *et al.*[31] also reported similar results for the transient decay characteristics of LB films of CuPc exposed to 120 ppm of NO_2 in nitrogen. The results reported by Sadaoka *et al.*[56] showed that the response times were less than 20 s and the recovery times were in the range of some minutes when using thin films of PbPc. The lack of reproducibility and the slow recovery time of these films are explained by the presence of large crystals in the conductive path.

The three main disadvantages of sensors based on films of PbPc which are addressed here are length of response time, humidity interference and possible chemical reaction at high NO_2 concentration. By altering the speed of gas exposure to the sensing film, the possibility of over-exposure to a high concentration of NO_2 can be avoided and therefore the risk of irreversible chemical reaction reduced. By optimizing the sensor operating temperature and the temperature and length of reversibility, decrease in the response to NO_2 due to the selective adsorption of the strong sites of the film can be avoided.[50, 57, 58] An exposure temperature of 150 °C gives a good measurable response and minimum humidity interference, while avoiding crowding of the strongest sites and hence a change in kinetics. Reversing at 200 °C for a

Table 1 Some parameters of semiconductive sensors for NO_2 based on phthalocyanines[a]

Phthalocyanine	Temperature (°C)[b]	Concentration range	Ref.
(t-b)$_4$NiPc	100	20–60 ppb	4
(CoPcCN)$_n$	100	5–500 ppm	4
PbPc	170	17–320 ppb	12
	247		8
	150	3.6–170 ppm	19
	150	40–100 ppb	46
	150	40–100 ppb	50
MPc (M=Co, Pb, Cu, Zn, Ni)	170	2.8–44 ppb	13
H_2Pc	170	0–50 ppb	13
MPc (M=H_2, Ni, Cu, Zn, Co, Mn, Pb)	—[c]	1–10 ppb	17
AlPcCl	200	3.6–170 ppm	19
AlPcF	200	3.6–170 ppm	19
CuPc	147	10–10^4 ppm	20
	150	1–50 ppm	28
CuPc[$CH_2NHCH(CH_3)_2$]$_3$		4–12 ppm	31
(AlPcF)$_n$	140–240	5–200 ppm	43
	120	20–200 ppm	45
ZnPc	200	1–100 ppm	38
MPc (M=Ni, Pb)		0–25 ppb	47
Crown-ether Pc[d]		1–5 ppm	48, 49

[a] Pc, phthalocyanine; (t-b)$_4$NiPc, tetra-t-butylphthalocyaninatonickel; (CoPcCN)$_n$, poly-[cyanotetracarboxyphthalocyaninatocobalt(III)]; AlPcF, fluoroaluminium phthalocyanine; AlPcCl, chloroaluminium phthalocyanine; (AlPcF)$_n$, poly(fluoroaluminium phthalocyanine).

[b] Room temperature is assumed if not specified.

[c] Temperature is not reported.

[d] 15-crown-5 phthalocyanine, 18-crown-6 phthalocyanine, 21-crown-7-phthalocyanine, and their KCl-treated thin coatings.

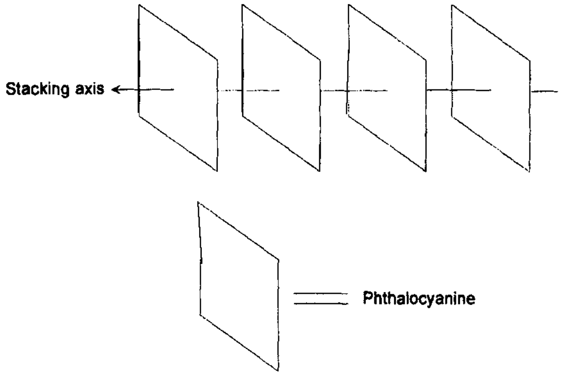

Figure 2 Metal phthalocyanine molecular stacking arrangement after doping.

period of time related to the exposure time gives good desorption of the NO_2 and a return to the optimal baseline value in a reasonable length of time on further reduction of the temperature to 150 °C. In addition, Sadaoka *et al.*[59] have found that the PbPc films, which transitioned to a crystalline form by annealing at 300 °C, exhibit at room temperature response times of less than 20 s and recovery times of the order of several minutes, independently of NO_2 concentration or exposure time. A similar result was also obtained by Wright *et al.*[20,58] after the PbPc films were treated at 360 °C for 1 h. The effects of NO_2 on the other MPcs [H_2Pc, PbPc, ZnPc, CuPc, AlPcCl, AlPc—O—AlPc and $(AlPc)_n$] films, which were treated in nitrogen at 350 °C, were also examined.[61] It was found that adsorption of NO_2 is limited to the surface of fine crystals and that the increase in the conductance caused by exposure to NO_2 is strongly influenced by the Pc crystallinity.

While only the responses to NO_2 have been reviewed and analysed here, other oxidizing gases, especially Cl_2, hydrogen sulphate (H_2S) and NH_3, can also be detected by using Pc-coated sensors.[7,27,35,36] Moreover, several other p-type organic compounds such as porphyrin,[7,46,62] annulene, perylene, tetracyaninoquinodimethane[8,17] and tetrapyrrole[62] have been also studied as semiconductive sensors for the detection of oxidizing gases.

2.2 Capacitance sensors

Although interdigital capacitors are widely used basic devices for capacitive chemical sensors due to their simple technology,[63] only one study has been reported so far,[64] in which Pc films were used as the chemical interface for organic vapours in air. The capacitance changes (ΔC) as determined using interdigital capacitors may result from changes of the relative dielectric coefficients ε_i in the gas phase ($l=1$), in the sensitive layer ($l=2$) and/or from the changes of the effective thickness (Δd) of the sensitive layer. Changes of the substrate-related dielectric coefficient ε_3 may be neglected.[11,65] In general, the dielectric coefficient of the substrate remains unchanged.

A typical time-dependence response of the interdigital capacitor coated with tetrakis(dodecylthio)phthalocyaninatonickel(II) ([(SR)$_4$PcNi]) exposed to chloroform is shown in Fig. 3. The sensor signals are reversible with response and recovery times of the order of a few minutes at room temperature. It is observed that the capacitance changes (ΔC) are linearly dependent on the analyte concentration. The capacitive sensitivities for different organic vapors investigated are given in Table 2. The capacitance sensor coated with [(SR)$_4$PcNi] showed higher sensitivity to organic molecules with a high dipole moment such as alcohols, acetone, dichloromethane and chloroform, and less sensitivity to organic molecules with small or zero dipole moment such as carbon tetrachloride, n-hexane and n-octane. However, it is observed that benzene, toluene and tetrachloroethylene with small or zero dipole moment showed reversible sensor signals. Such a

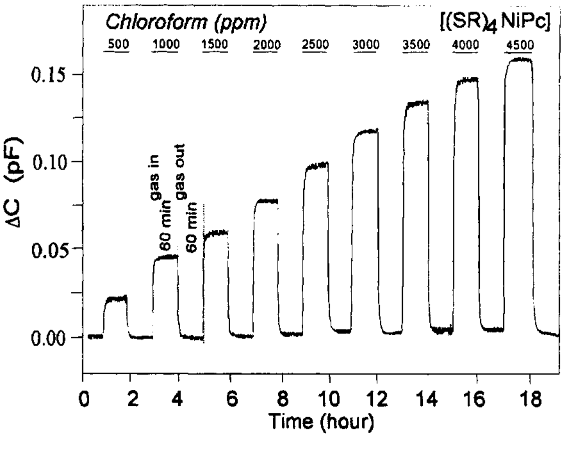

Figure 3 Typical capacitance changes ΔC of the interdigital capacitor sensor coated with [(SR)$_4$PcNi] as a function of time for stepwise exposure to different concentations of chloroform in air at room temperature. (Reprinted from *Sensors & Actuators* **B26–27**, Z. Z. Öztürk *et al.*, pp. 208–212 (1995), with kind permission from Elsevier Science S.A., Lausanne, Switzerland.)

Table 2 Capacitive sensitivity of $[(SR)_4PcNi]$- and $[(SR')_4PcNi(PdCl_2)_2]$-coated IDC sensors for various organic solvent vapours[a]

Organic solvent	Capacitive sensitivity $\Delta C/p_g$ (10^{-15} F Pa^{-1}) $[(SR)_4PcNi]$	$[(SR')_4PcNi(PdCl_2)_2]$	Dipole moment (D)
Acetone	0.0234	0.0214	2.69
Benzene	0.0106	0.0125	0.00
Toluene	0.0258	0.0282	0.31
Dichloromethane	0.0233	—[b]	1.14
Chloroform	0.036	0.0307	1.15
Carbon tetrachloride	0.00796	—[b]	0.00
Trichloroethylene	0.0285	0.0256	0.80
Tetrachloroethylene	0.0209	0.0204	0.00
Methanol	0.0118	0.0188	2.87
Ethanol	0.0135	—[b]	1.66
n-Propanol	0.0392	—[b]	3.09
n-Hexane	0.00179	—[b]	0.09
n-Octane	—[b]	—[c]	0.00

[a] Adopted from Ref. 64; $[(SR)_4PcNi]$, tetrakis(hexylthio)phthalocyaninatonickel; $[(SR')_4PcNi(PdCl_2)_2]$, palladium(II) complex of tetrakis (dodecylthio)phthalocyaninatonickel.

[b] Not measured.

[c] Less sensitive.

response can be explained by dipole-induced/dipole-induced interactions.[11,66] Similar results were obtained for the capacitance sensor utilizing the planar polymer film of $[(SR)_4PcNi]$, prepared by its palladium(II) complexation.

2.3 Sensors based on field-effect transistors (FET)

Interdigitated gate-electrode field-effect transistor (IGE–FET) sensors offer an alternative technology concept for detecting gaseous contaminants when coupled with an appropriate chemically active film.[67] By extension, an array of discrete IGE–FETs, each supporting a different chemically active layer, coud be electronically multiplexed to measure different species. It is believed that these arrays can widely be applied in multicomponent analysis with chemometrics.

Burr *et al.*[68] fabricated a more sensitive NO_2-responsive transistor by thermally evaporating a thin layer of PbPc over the gate oxide region of an FET. It was found that the very long response times (several days) exhibited by this FET device at NO_2 concentrations below 10 ppb precluded its operation as a sensor for parts-per-billion ($1{:}10^9$) levels of the gas. It is interesting to note that a plot of threshold voltage V_t vs $[NO_2]$ on a logarithmic scale was linear with a slope of 395 mV per decade over the concentration range 20–1000 ppb, but the device was capable of responding to levels of the gas below 20 ppb.

Schoch and Tenofonte[9] also used an FET sensor structure to perform measurement of gas species with comparable sensitivity but lower noise at room temperature using H_2Pc and MPc (M = Cu, Ni, Pb) as the sensitive materials. In this study, the films prepared by evaporation are very sensitive, have fast responses at room temperature and are more mechanically durable. Recently, an IGE–FET coupled to an electron-beam-evaporated film of CuPc was used to detect parts-per-billion concentration levels of NO_2 selectively.[69] The sensor was excited with a voltage pulse, and with the time- and frequency-domain responses were measured. The envelopes of the magnitude of the normalized difference frequency spectra reveal features that unambiguously distinguish NO_2 exposures. For a CuPC film 1.0×10^{-7} m thick, a reversible response to NO_2 was achieved when the IGE–FET was operated at 125 °C.

There are two recent examples of FET incorporating LB films of Pcs.[70,71] Gu and Sun[71] reported a selective NO_2-sensor based on FET using an LB film of copper *t*-4-(2,4-di-t-amylphenylsulphonyl)phthalocyanine. The FET coated with LB film was sensitive to NO_2 at 1–10 ppm, but insensitive to NH_3, H_2S, CO and ethanol. If this approach is to be used commercially, it will be essential to add some intelligent feature to improve their discrimination capabilities, i.e. multiplexing using a number of different devices and operations under different conditions.[30]

2.4 Solid-state ionic sensors

Solid-state ionic sensors have been widely applied to detect ions and gases in aqueous, organic and gaseous states. However, only a very few NO_2 solid-state ionic sensors utilizing phthalocyanine films as sensitive materials have been reported. Göpel *et al.*[72–77] first proposed a monitor of NO_2 and O_2 in the gas phase with a potentiometric cell (Fig. 4).

In the system AgI/PbPc, the mixed conduction of PbPc (O_2^-, I_2^- and defect electron conduction) and the ionic conduction of AgI are utilized to measure changes in the overall voltages of the electrochemical cell upon changes in NO_2 and O_2 concentrations. A detailed analysis of the potential response indicates that NO_2 is detected by a reaction with I_2^- followed by diffusion through the PbPc to the outer PbPc/C/gas three-phase boundary.[1] O_2 on the contrary, is monitored by potential variations at the inner Ag/PbPc interface by an equilibrium reaction with I^-.[72] It was indicated that the interaction mechanism can be easily understood with this system and a sensing mechanism of the optimized sensor structure by an atomic interpretation was proposed.

3 MASS-SENSITIVE SENSORS

Since King[78] first introduced the quartz crystal microbalances (QCM) as detectors in gas chromatography on the basis of the Sauerbrey equation ($\Delta f \propto \Delta m$, where Δf is the change in resonant frequency and Δm the change in the attached mass),[79,80] a variety of other mass-sensitive devices have been utilized to create mass-sensitive sensors. These mass-sensitive devices include surface acoustic-wave,[81] flexural-plate wave[82,83] and shear horizontal acoustic plate-mode devices,[83–86] and an electrochemical quartz crystal microbalance.[83,87] These devices, characterized by a relatively high sensitivity that is a function of operating frequency and crystal thickness, have a low detection limit, a broad application range in both gas and liquid phases, and a continuous-operation model.[1,11,88–90] Only quartz crystal microbalance (QCM) and surface acoustic-wave (SAW) sensors which are mostly used to detect NO_2 and organic vapours with Pc films, will be discussed here.

3.1 Quartz crystal microbalance (QCM) sensors

QCM sensor for NO_2

NO_2 sensors using QCM devices coated with Pc layers were reported by Zhou *et al.*[4,91] The objective was to develop long-term stable and sensitive low-temperature sensors for NO_2 in air. Unfortunately, the device response showed a baseline drift. To eliminate the baseline drift effect, a differential method for response measurement was proposed.[4,11,91] Typical differential sensor signals are shown in Fig. 5, in which the differential baseline is stable and the sensor response is reversible. The sensitivity properties of some monomeric and polymeric Pc films investigated for NO_2 at room temperature are represented in Table 3.

Monomeric tetra-t-butyl phthalocyaninatonickel [$(t\text{-Bu})_4$NiPc] as QCM sensor interface films show typical detection limits of the order of 50 ppm NO_2 in air at room temperature with reversible sensor signals. Although a poly[cyano(cobalt tetracarboxyphthalocyanine)] [$(\text{CoPcCN})_n$] layer can be used to monitor NO_2 gas at a concentration greater than 1 ppm at room temperature, no linear dependence is observed and the response cannot be reversed at the same temperature. Reversible sensor signals are only obtained after heating to a higher temperature (100 °C) for several minutes.

Polymer-bound Pcs are less sensitive to NO_2 than the monomeric and electronegative polymeric Pcs. Also, copper-containing polymers with polystyrene as the polymer backbone are more sensitive than the cobalt-containing polymers. It is noted that the sensor's resonance frequency changes usually did not return fast enough to the initial value at room temperature. However, this reversibility could always be achieved by heating to 100 °C for several minutes after a series of measurements, in which

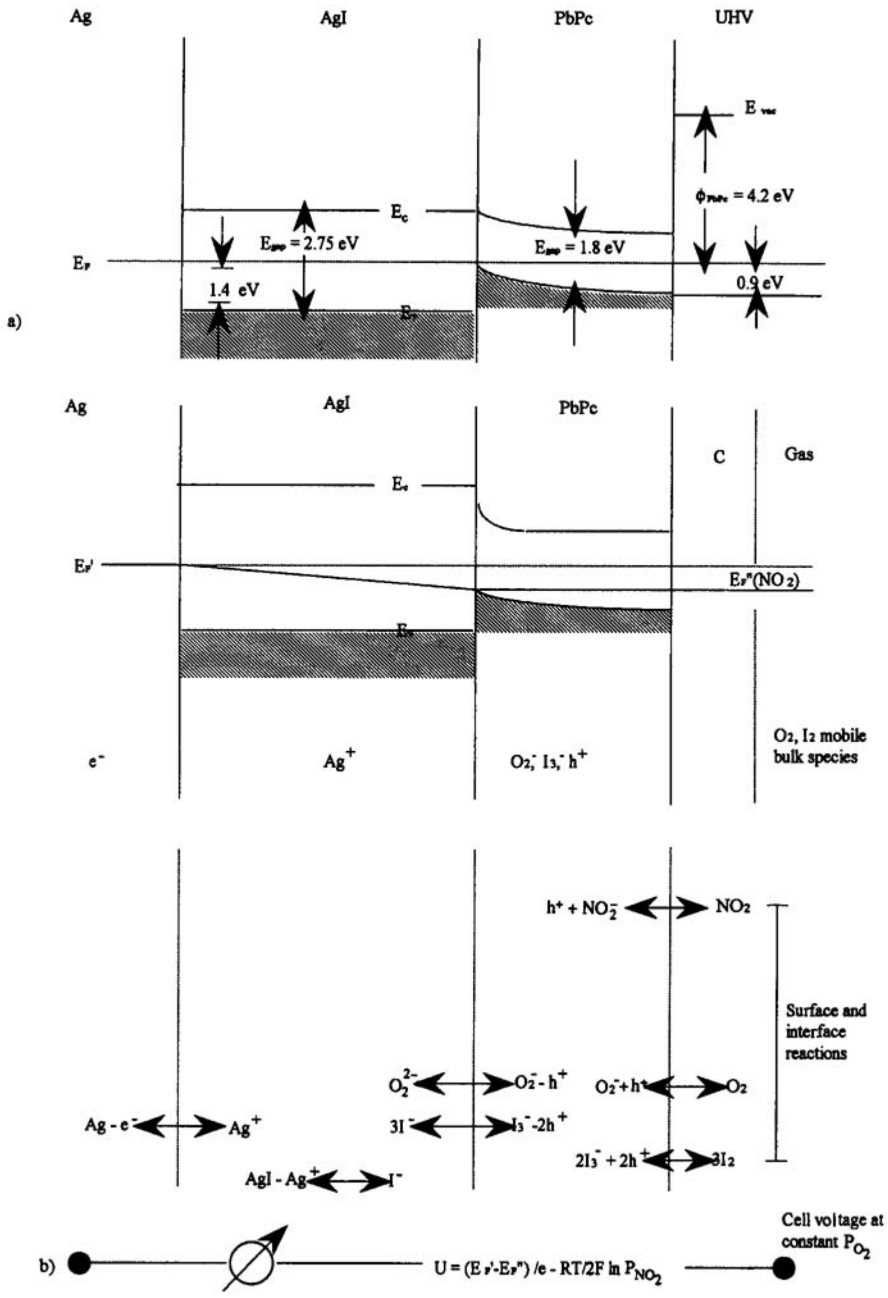

Figure 4 Schematic diagram of a potentiometric cell to monitor O_2 and NO_2 in the gas phase. The sandwich structure makes use of electron conduction (e) across the contacts Ag and C, ionic conduction (Ag^+) in AgI and conduction (O_2^-, I_3^-, h^+) in PbPc. (a) is the uppermost part, which consists of the positions of occupied and empty electronic states including the valence band E_v, conduction band E_c, the bandgap E_{gap}, work function ϕ and Fermi level E_F; (b) is the lowest part which determines NO_2 or O_2 gas atmosphere conditions in the electrochemical cell. The lower parts describe the chemical composition, geometric structure, mobile bulk species, and interfaces with trapped species (O_2^{2-}, I^-, NO_2^-). (Reprinted from *Synthetic Metals* **41/43**, W. Göpel, p. 1087 (1991), with kind permission from Elsevier Science S.A., Lausanne, Switzerland.)

the d*f*/d*t* value can be correlated unequivocally to NO_2 concentration.

Other Pc films such as the crown-ether Pcs and the planar polymer of [$(SR)_4PcNi$] have also been investigated as a chemical interface for QCM.[48,49,64] Results have shown no reversibility for these sensors coated with crown-ether Pcs[92] and good reversibility, high sensitivity and long-term stability for those coated with the planar polymer of [$(SR)_4PcNi$].[64]

QCM sensors for organic solvents

Phthalocyanines have also been studied as sensitive films for the detection of organic vapours.[64,91,93-96] Korosawa *et al.* studied the sensitivities of CuPc, which was plasma-polymerized on QCM devices, for a variety of organic chemicals in the gas phase. The results indicated that the films were very stable, behaved identically to chemical and physical treatment and were sensitive to many organic chemicals. They were especially sensitive to planar molecules having conjugate double bonds and some polar substituting groups or higher alcohols, such as vanilin, benzoic acid, aniline, nitrobenzene, phenol, n-octanol, l-nonanol, n-decanol, DL-camphor, β-ionone, naphthalene and anthracene. In addition, the results showed that the sensitivities to various chemicals were dependent on the central metal of the Pc.

Zhou *et al.* studied sensor properties of different monomeric and polymeric Pcs for the detection of organic solvents.[11,91,94] The results, as reported for NO_2 sensors,[64,94] showed some baseline drift for the polymeric Pcs such as polymer-bound MPcs. However, some of the soluble monomeric Pcs, such as $(t\text{-}Bu)_4NiPc$, showed very stable and sensitive sensor signals. On that basis, different soluble Pcs have been investigated as sensitive materials for organic vapours.[64,96] Typical results on the time dependence of frequency changes (Δ*f*) during solvent molecule/Pc interactions are shown in Fig. 6 for different concentrations of chloroform exposed to octaheptylphthalocyaninatocobalt(II).

The new class of modified Pcs which are substituted with large organic side groups and hence have higher solubilities in organic solv-

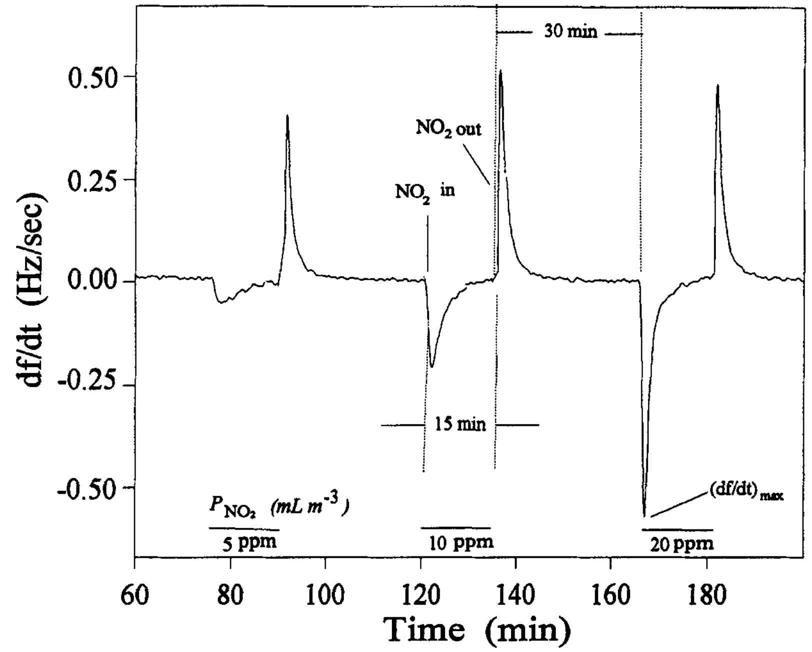

Figure 5 Typical results of frequency changes as a function of time (d*f*/d*t*) in a sequence of NO_2 exposures and pump-down experiments. In all experiments, exposure times and pump-down times were the same. Polymer: poly(4-vinylpyridine-*co*-styrene)-bound dicarboxyphthalocyaninatocopper(II)). (Reprinted from *Sensors & Actuators* **B15–16**, R. Zhou *et al.*, pp. 312–316 (1993), with kind permission from Elsevier Science S.A., Lausanne, Switzerland.)

ents show, by far, better properties (response and recovery times, stabilities) than insoluble phthalocyanines.[11,91,94] Soluble tetrakis(alkylthio)phthalocyaninatonickel(II) and its planar polymers through complexes with palladium(II) and silver(I) were used as sensitive films to detect and quantify organic vapours in air.[64] The chemical structure of the palladium(II) complexes of tetrakis(alkylthio)phthalocyaninatonickel(II) is illustrated in Fig. 7. Like the other soluble Pcs, these sensors showed high sensitivity, reversible response and long-term stability.

An overview of the soluble Pcs used for the detection of organic solent vapours is given in Table 4. In our studies, sensitivity is defined as the series resonant frequency change Δf divided by the analyte concentration, c, with respect to the difference (Δf_d) of the oscillation frequencies of uncoated and coated quartz oscillators.[11,67,96] This definition of the sensitivity is related to the mass of the Pc films and hence to the number of Pc macromolecules ('recognition sites'). The differences in the molecular weights of the Pcs may be neglected here to a first approximation. The pronounced changes in sensitivities may be explained in terms of differences in the boiling temperature of different organic molecules.[11,64,96] From this, it may be concluded that molecule/MPc interactions are mainly determined by van der Waals bond energies between polarizable aromatic rings of the Pc and the molecules. Specific interactions involving electronic states of the central metal may play only a minor role. However, the strong sensitivities of the metal-free $(t\text{-Bu})_4PcH_2$ towards alcohols with their hydroxyl group (OH) is greatly suppressed if the Pc ring contains a central metal atom (see results in Fig. 8 and Ref. 96).

However, no evidence can be derived from our

Table 3 Sensitivity properties of coatings with monomeric, polymeric and polymer-bound phthalocyanines: initial slopes of frequency changes divided by the NO_2 concentration (sensitivity) of quartz microbalance devices operated at room temperature[a]

Sensitive material	Thickness (μm)	Minimum detection limit (ppm)	Sensitivity (Hz s ppm^{-1})
Nickel-t-butyl phthalocyanine	0.08	50	0.00064
Poly[cyano(cobalt tetracarboxyphthalocyanine)]	0.37	1	—[b]
Polystyrene-bound cobalt tetracarboxyphthalocyanine	0.47	5	0.046
Polystyrene-bound copper tetracarboxyphthalocyanine	0.28	5	0.0055
Poly(4-vinylpyridine-*co*-styrene)-bound cobalt tetracarboxyphthalocyanine	0.52	5	0.046
Poly(4-vinylpyridine-*co*-styrene)-bound copper tetracarboxyphthalocyanine	0.40	5	0.028
Polystyrene-bound cobalt dicarboxybenzoylphthalocyanine	0.70	50	0.011
Polystyrene-bound copper dicarboxybenzoylphthalocyanine	0.35	70	0.032
Poly(4-vinylpyridine-*co*-styrene)-bound copper dicarboxybenzoylphthalocyanine	0.63	50	0.00053
Poly(4-vinylpyridine-*co*-styrene)-bound copper dicarboxybenzoylphthalocyanine	0.53	5	0.036

[a] Adopted from Ref. 4.

[b] Unstable behaviour.

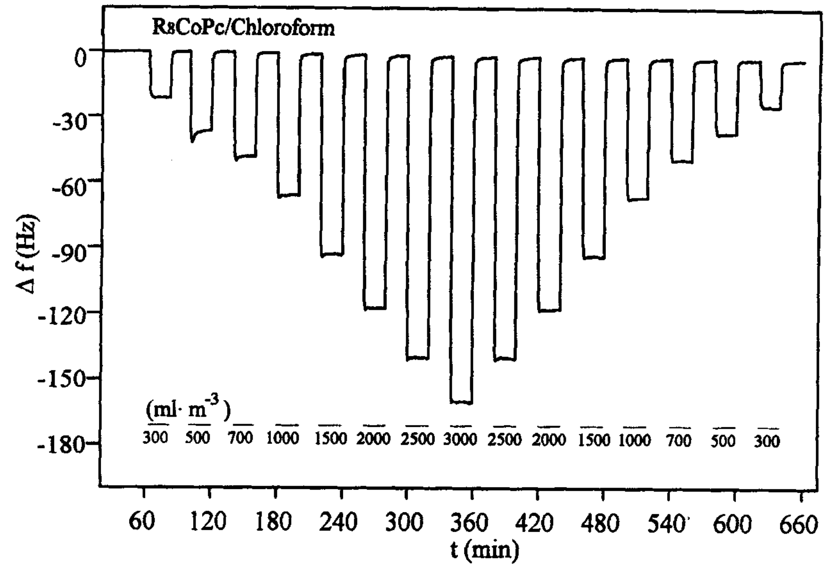

Figure 6 Typical examples of frequency changes Δ*f* of quartz crystal microbalance sensors. Here, R_8CoPc layers were exposed to different concentrations of chloroform in air at room temperature.

experiments for possible metal/molecule interactions involving, for example, metallic electronic states and π-bonds of the molecules. This is because sensitivities are also different for nonpolar and nonpolarizable molecules like n-hexane and n-octane.[64, 96] Therefore, it is concluded that the central metal atom affects the electronic polarizabilities of the aromatic rings of the Pcs. This changes the van der Waals interaction energies and hence the sensitivities of the MPc-coated sensors. Of particular relevance for practical applications is the extremely high sensitivity of $(PPO)_4PcCo$ towards tetrachloroethylene. In this case, the sensitivity is larger than those of 'simpler' polymers such as poly(dimethylsiloxane)[96, 97] by one order of magnitude.

It should be noted that in those QCM sensors, only the change in the series resonant frequency was measured. This implied that only sensitivity based on mass loading is being quantified. However, changes in conductivity in Pc films upon interaction with the gas molecules could be investigated utilizing quartz crystal resonators (QCRs)[98] for high sensitivity or selectivity.

3.2 SAW sensors

Since Wohltjen and Dessy[99] extended the detection principle from the quartz crystal microbalance to surface acoustic waves (SAWs), SAW devices have been widely used as sensing devices for the detection of chemicals.[100] In these devices, an appropriate selective, sensitive film is used as a chemical interface on a delay line. In general, a dual delay line configuration is employed in sensor applications, in which the second delay line is used as a reference line to compensate for or eliminate second-order effects such as temperature and pressure variations. Nieuwenhuizen *et al.*[101, 102] first utilized an SAW delay line coated with Pc films for the detection of NO_x. Examples of parameters of SAW sensors for NO_2 based on Pc films are given in Table 5.

These Pc films offer two sites for interaction, one at the metal ion (coordination complex formation) and one at the electron cloud at the periphery of the molecule (charge-transfer complex formation).[101] From the results in the Table, the response times are still rather long for sensor applications. This problem could be solved by using thinner films which will lead to shorter response times. A corresponding decrease in sensitivity might be compensated by operating the sensor at higher frequencies. Also, higher temperatures might be applied to reduce the response times. However, this approach is limited by the physical stability of Pc films. Further development has been achieved by using a two-step procedure with a so-called spacer

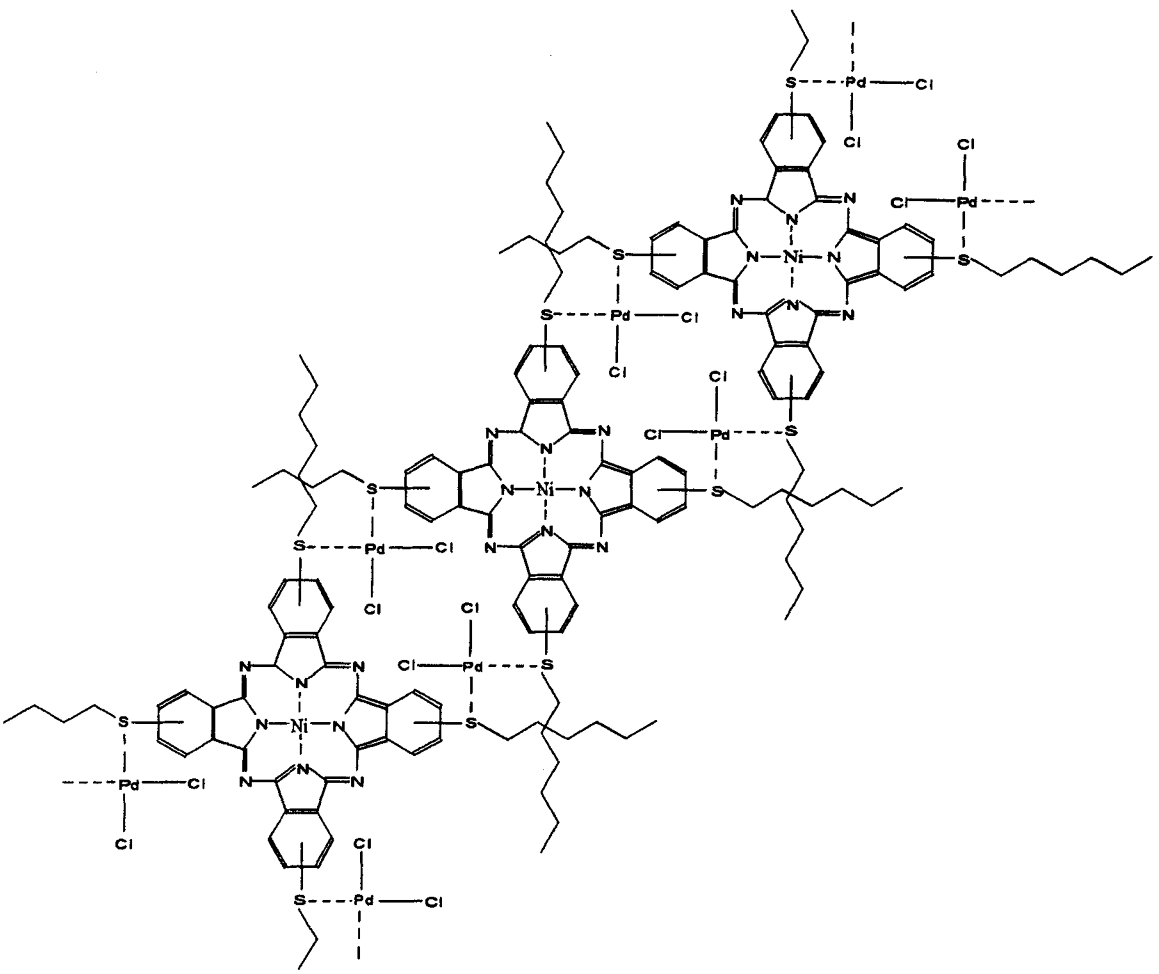

Figure 7 Assumed chemical structure of the Pd^{II} complex of $[(SR')_4 PcNi(PdCl_2)_2]$. (Reprinted from *Sensors & Actuators* **B26–27**, Z. Z. Öztük *et al.*, pp. 208–212 (1995), with kind permission from Elsevier Science S.A., Lausanne, Switzerland.)

molecule.[101, 107] The spacer molecule, such as 3-aminopropyltriethoxysilane, has, at one end, a group that is sufficiently reactive to react with the oxidic detector surface (triethoxy groups) and, at the other end, an amino group which reacts with the chemical interface molecule, e.g. copper tetracarbonylchloride phthalocyanine.[101, 107] With the spacer concept, the reactivity of the surface is enhanced by introducing amino groups which can easily react with carboxylic groups in the Pc derivative. Access to the surface is then inceased by the spacer molecules rising out of the surface. The results showed that the response time is shortened, whereas the sensitivity is decreased. This decrease of sensitivity may be caused by the decrease of the number of the Pc molecules in the film compared to the other films.

It is worth noting that the results indicated that PbPc cannot be used due to irreversible effects, and it was concluded that the transduction mechanism of SAW chemosensors is a combination of changes in mass and conductivity.[100]

Differences in NO_2 sensitivities and in the response time between air and nitrogen were observed and the influence from NO, CO and O_2 was investigated.[100] NO reacted with the Pc or changed its morphology in the same way as NO_2, because changes in the behaviour of the sensor coating were observed after exposure to NO. The results for the system NO in nitrogen (N) indicated the formation of coordination compounds. Its effect in air mainly results in the formation of NO_2 in oxidizing atmospheres and

Table 4 Overview of quartz crystal microbalance (QCM) sensors coated with phthalocyanines used for organic analytes

Phthalocyanine layers	References
Tetra-t-butylphthalocyaninatometal(II) (metal = H_2, Co, Ni)	4, 94, 96
Tetrakis(2,2-dimethyl-3-phenylpropoxy)phthalocyaninatometal(II) (metal = H_2, Co, Cu, Fe, Ni)	96
Octaheptylphthalocyaninatometal(II) (metal = Co, Ni)	96
Tetrakis(hexylthio)phthalocyaninatonickel(II)	66
Tetrakis(dodecylthio)phthalocyaninatonickel(II)	64
Palladium(II) complex of tetrakis(dodecylthio)phthalocyaninatonickel(II)	64
Silver(II) complex of tetrakis(dodecylthio)phthalocyaninatonickel(II)	64
Plasma-polymerized phthalocyaninatocopper(II)	95
Poly[cyano(tetracarboxyphthalocyaninatocobalt(III)]	4, 94
Polystyrene-bound tetracarboxyphthalocyaninatometal(II) (metal = Co, Cu)	4, 11, 91, 94
Polystyrene-bound dicarboxybenzoylphthalocyaninatocopper(II)	4, 11, 91, 94
Polystyrene-bound dicarboxybenzoylphthalocyaninatocopper(II) dimer	
Poly(4-vinylpyridine-*co*-styrene)-bound tetracarboxyphthalocyaninatometal(II) (metal = Co, Cu)	4, 11, 91, 94
Poly(4-vinylpyridine-*co*-styrene)-bound dicarboxybenzoylphthalocyaninatometal(II) (metal = Co, Cu)	4, 11, 91, 94

nitrogen, possibly enhanced by the catalytic effect of Pcs as well as high temperatures and metal surfaces of the measuring cell. CuPc is insensitive to CO or O_2 at 150 °C, while FePc

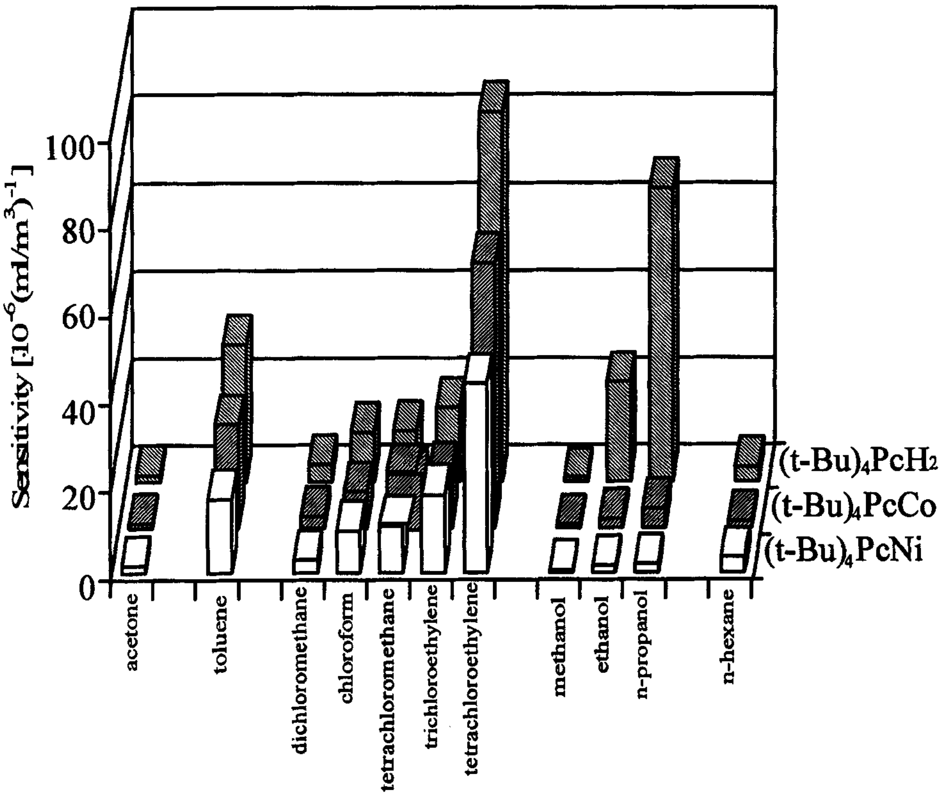

Figure 8 Sensitivities of $(t\text{-Bu})_4H_2Pc$, $(t\text{-Bu})_4CoPc$, and $(t\text{-Bu})_4NiPca$ for different solvent molecules in air at $T = 298$ K. (Reprinted from *Sensors & Actuators* **B24–25**, K. D. Schierbaum *et al.*, pp. 69–71 (1995), with kind permission from Elsevier Science S.A., Lausanne, Switzerland.) (See text for the definition of sensitivities.)

Table 5 Some parameters of SAW sensors for NO_2 based on phthalocyanine layers investigated[a]

Phthalocyanine layer	Temperature (°C)	Concentration range	Refs
PbPc	80	0–10 ppm	10
	120	25 ppb–ppm range	105
CoPc	150	40–160 ppm	101, 103
CuPc	120	ppm range	105
MPc (M=Cu, Fe, Mg, Ni, H_2)	150	20–200 ppb	101, 103
Tetra-4-butylsilicon phthalocyanine dichloride	—[b]	1.5–40 ppb	104
Tetrasulphonated CuPc		0–12 ppm	106

[a] Pc, phthalocyanine.

[b] Room temperature is assumed.

shows only initial effects. At lower temperatures (down to 30 °C), very low sensitivities were observed. Halogen gases showed a strong interference with sensitivity and stability, confirming the strong interaction of electronegative compounds with Pcs.

The application of LB coatings of phthalocyanines as gas-absorbent films on the surface of SAW devices was also reported.[104] The room-temperature chemiresponse of a SAW sensor, which was coated with monolayers of tetra-t-butylsilicon Pc dichloride, showed response and recovery times comparable with those reported for other Pc-based sensors operated at much higher temperatures. A SAW delay line oscillating at a relatively high frequency in this experiment has shown a detection limit of 0.5 ppb for NO_2 for an 11-layer Pc device, but with reduced response times due to the ultrathin nature of the film. In general, the change in mass due to gas adsorption and the conductivity change in the Pc film both contribute to the SAW gas sensor response. While it is often difficult to separate the effect of each contribution in an actual device, a specific device can be designed which will enhance only one transduction mechanism. For example, a thin film of a conductive film (aluminium, gold) could be used to eliminate any electrical loading effect. Such films will short out the electric field associated with the propagating acoustic wave and hence eliminate any possible effect of conductivity change in the Pc film. On the other hand, the SAW device could be designed on a $LiNbO_3$ substrate, a relatively strong piezoelectric coupling material, and conductivity changes in a PbPc thin surface coating of the device can be used as the basis for a SAW gas sensor.[108] It is evident that the sensitivity of this particular SAW sensor on $LiNbO_3$ is approximately 1000 times greater than that of an identical system relying on mass loading alone. Such a SAW sensor can be used to measure a few parts per million of NO_2 in nitrogen.[108] To utilize conductivity changes, the sensing mechanism could be expected to behave somewhat differently from a resistance-measuring sensor using the same coating, in terms of repsonse time and dependence on coating thickness. A SAW sensor based on a $ZnO–SiO_2–Si$ Pc film was shown to be more temperature-stable and more sensitive than a quartz-based system.[109] Finally, it is interesting to point out that mass and conductivity are not the only physical parameters that can be detected. The elastic properties and photoconductivity of the overlay can also be used advantageously in such devices. However, one must be careful in designing such sensor devices, since the viscoelastic effect tends to also oppose the mass loading effect.

Nieuwenhuizen *et al.*[109] proposed a number of mechanisms which influence the velocity of the interaction between NO_2 and Pc and thereby the response time. One of these mechanisms is the completion of the formation of a charge-transfer complex:

$$NO_2 + H_2{—}Pc \rightleftharpoons NO_2{—}H_2{—}Pc$$

and consists first of a layer diffusion at the surface of the Pc film, followed by a possible pore diffusion when the surface characteristics necessitate it. Finally, equilibrium is reached after a period of time. Moreover, in some special cases, another kinetic complication may occur with the transformation of NO_2 to N_2O_4. When the NO_2 is withdrawn the replenishment by dissociation of N_2O_4 will take some time. This problem can be solved when the operating temperature is greater than 100 °C because almost all N_2O_4 will be dissociated at this temperature.

4 OPTICAL PROPERTIES

In previous studies of Pc-based sensors where the conductive response of Pc-coated sensors to NO_2 was determined,[7] reversible changes in the IR transmission of the layers were observed. It is therefore apparent that the adsorption of NO_x by a Pc film exposed to a high concentration of the gas for a few seconds can be studied by transmission IR spectroscopy.

In 1988, Schoch and Temofonte[9] reported the IR response to NO_2 of NiPc and PbPc thin films deposited on NaCl crystals and the possibility of detecting NO_2. The IR transmission of thin Pc films decreases dramatically after exposure to NO_2 at room temperature. This effect is caused by the creation of carriers and is concurrent with increased electrical conductivity of the films. It was indicated that both effects can be reversed by heating the films to 160 °C in vacuum. At gas concentrations below approximately 1800 ppm, the absorbance is directly proportional to gas concentration. An optical detection limit of 100–200 ppm NO_2 in air was observed for PbPc film, compared with an electrical detection limit of 1–10 ppb in air, thus making the observed optical response less striking. However, it is worth noting that the response is linear at least up to 1800 ppm, with an optical detection limit of the order of 1 ppm. In addition, Schoch *et al.*[110] discussed the optical response of several MPc ($M=H_2$, Cu, Ni, Pb) thin films to NO_2. The results showed that the IR response to NO_2/air mixtures can be detected at room temperature.

One possible explanation for the differing electrical behaviour pertains to the anisotropy of the crystal structures in the film.[110, 111] Electrical conductivity is much higher after NO_2 oxidation in the direction parallel to the long axis of the needle-like MPc crystals. Electrical measurements were made in a direction parallel to the needle axis, whereas the optical measurements were averaged over all orientations through the bulk of the layer. Consequently, the optical measurement would include some of the less sensitive directions n the MPc films.

The relation between electrical conductivity and thermal desorption spectra for CoPc/oxidative gas systems is discussed in Ref. 112. The results have shown that the CoPc/O_2 system gives a single desorption peak in the temperature range 40–100 °C, while CoPc/NO and CoPc/NO_2 show desorption in two steps, the first at 50–100 °C and the second at 100–300 °C. The first and second peaks were assigned to the desorption of NO_2 on the pseudoaromatic ring and on the cobalt ions, respectively. This is consistent with the fact that the electrical conductance increases when NO_2 is adsorbed on the pseudoaromatic ring of the Pcs, while NO_2 adsorption on cobalt ions does not affect the conductance.

The influence of thin films of PbPc, humidity and NO_2 concentration on the sensor signal has been discussed on the basis of FT-IR, IR, X-ray diffraction and UV/VIS spectrometric data.[31, 58, 113–117] A pronounced difference in the sensor signal is caused by a variation of the chemical structure of thin films. The expected behaviour of the humidity dependence was only obtained during the first 30 min. Thereafter, the sensor current increased up to a final value which was about 20% higher than the value in the absence of water for 75% relative humidity, and was 14% higher for 100% relative humidity.

In another study utilizing a surface plasmon resonance technique, Lloyd *et al.*,[118] using a substituted Pc LB film, showed good sensitivity and linear range up to 1000 ppm NO_2. Souto *et al.*[119] investigated the sensing properties of the MPc (M=Co, Ni, Cu) for NO_2 using UV/Vis, FTIR and Raman spectroscopies. The result showed reversible signals for NiPc and CuPc films. Moreover, Souto *et al.*[119] studied the sensor properties of the lanthanide phthalocyanines such as praseodymium, gadolinium, ytterbium diphthalocyanines and octa-t-butyl praseodymium diphthalocyanine for the smoke gases using UV/Vis and Raman spectroscopies. The effect of the smoke gases on the Pc films is based on the temporary change of colour from the unreduced green starting materials to a blue reduced layer. Satisfactory results were obtained from the different LaPcs.

In addition, different porphyrins have been also used as optical sensors for the detection of NO_x.[117, 120–124] On the basis of these results, the degree of resistance to chemical attack of organic layers exposed to strong oxidizing agents like NO_x was estimated, and evidence for the mechanisms of interaction between the organic films and the reactive gas was found.[125] It was suggested that, as the time of exposure to NO_x increases, partially empty valence levels of the organic molecules become completely empty, thereby removing the charge carriers. Furthermore, the sheer physical impediment of the charge transport processes by bulk-physisorbed gas will also diminish the surface conductivity. This is in acordance with the observations that, although small quantities of NO_x lead to a pronounced enhancement of surface dark d.c. current across a porphin film, massive exposure to NO_x produces an insulating surface with a conductivity similar to that of the original clean material. It is possible to regenerate a clean film suitable for detecting low levels of NO_x only in the cases of the porphyrin free bases. Regeneration is achieved by heating slowly to 100 °C.

5 CONCLUSIONS

Single-crystal and polycrystalline layers of phthalocyanines have a high sensitivity to NO_x and halogens, with the sensitivity being a function of the film thickness. However, the thickness and reproducibility of the films are not easy to control. The Langmuir–Blodgett (LB) technique offers excellent control over film thickness and reproducibility; however, the LB film is quite fragile and its sensitivity is rather low compared with sublimed films. Moreover, insoluble nitrogen-containing macrocycles cannot be applied as LB films, thus limiting the potential application of the LB technique in sensors. Smearing film does not produce homogeneous films.

Semiconductive sensors have been widely studied for NO_x detection because the response can easily be recognized and the sensitivity is very high. Photoconduction of phthalocyanines is more sensitive to low concentration than is semiconduction. However, these effects are much more difficult to reverse than the effects of the same gases on semiconductivity. SAW devices are attractive for chemical microsensor applications because of their small size, low cost, high sensitivity and good reliability, but they are less sensitive than chemiresistor-based sensors. Surface dark d.c. current is the most reversible physical property, whereas a device based on measuring such a quantity is very complicated to achieve. With FET devices, it is possible to determine simultaneously different gases in the same sample, but selectivity is low. Although there are only a few studies utilizing QCM devices and solid-state ionic sensors, preliminary results indicate that further studies should be conducted on NO_2 sensors with phthalocyanines as sensitive coating materials. Such studies should also include the use of quartz crystal resonators (QCRs) with modified electrode geometry as effective detectors of conductivity and dielectric constants.

In summary, phthalocyanines and their metal complexes have been confirmed to be very suitable coating materials for gas-sensing devices, which can be used to detect NO_2 in practically relevant concentrations. However, the studies also show that these types of sensors are still in their infancy and the great majority are still in the laboratories. Therefore, the development of practical, sensitive, selective and stable gas sensors for environmental chemistry applications is still a task to be accomplished.

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