INVESTIGATION OF THE SENSITIVITY,
SELECTIVITY, AND REVERSIBILITY OF THE
CHEMICALLY-SENSITIVE FIELD-EFFECT TRANSISTOR (CHEMFET)
TO DETECT NO_2 , $C_3H_9PO_3$, AND BF_3

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ABSTRACT

The sensitivity, selectivity, and reversibility of a CHEMFET gas microsensor were investigated as a function of several physical operating parameters. The CHEMFET's responses were expressed based upon the changes generated by modulating the electrical conductivity of the microsensor's thin-film, metal-doped, phthalocyanine-coated interdigitated gate electrode when exposed to a family of challenge gases. The operating parameters included: chemically-sensitive thin-film composition and thickness, challenge gas specie and concentration, and ambient temperature. Copper phthalocyanine (CuPc) and lead phthalocyanine (PbPc) were used as the chemically-sensitive thin-films which ranged in thicknesses from 250 Å to 1100 Å. The challenge gases included: nitrogen dioxide (NO_2), dimethyl methylphosphonate ($C_3H_9PO_3$), boron trifluoride (BF_3), methanol (CH_3OH), carbon monoxide (CO), vinyl chloride (CH_2CHCl), and trichloroethylene (C_2HCl_3). The concentrations of the gases ranged from 10 parts-per-billion (ppb) to 50 parts-per-million (ppm). Tests performed at 22°C and 110°C (70°C for the latter four gases) revealed that CuPc was more sensitive to $C_3H_9PO_3$ and BF_3 , whereas PbPc was more sensitive to NO_2 , CH_3OH , CO , CH_2CHCl , and C_2HCl_3 . The CHEMFET was also moderately selective when challenged with several bi-

nary challenge gas mixtures. The metal-doped phthalocyanine thin films were most selective to NO_2 , followed by $C_3H_9PO_3$. The CHEMFET was not as selective for BF_3 when combined with several other challenge gases. The CHEMFET was totally reversible for both thin-film candidates and all challenge gases.

I. INTRODUCTION

Our rapidly developing world is confronted with many environmental challenges. The efforts to maintain and improve the "standard of living" from a technological perspective has resulted in the contamination of the air, water, and land. Exposing the environment to toxic chemicals has threatened the living and working conditions of man. Prior to the past decade, technological innovations for monitoring and protecting the environment have been limited.

Increased concern for the health and safety issues involved with degrading the environment has prompted the development of technologies to detect, quantify, monitor, and remediate environmental toxins. As progress is achieved in some areas, new problems are discovered; these new environmental challenges tend to involve less visible pollutants, that are also more persistent. Emissions into the air and water may persist for decades. Furthermore, numerous

chemical compounds, once thought to be harmless, have now been determined to be toxic, even in trace amounts.

Many hazardous chemical compounds are in the form of gases or vapors. The detection and measurement of these gases and vapors in the atmosphere, as well as in closed ecological systems, have merited significant attention. Much of this attention has been focused on health and safety issues, primarily through additional restrictive federal regulations, and the economic liabilities for non-compliance are becoming more influential.

The military is particularly interested in detecting and monitoring regulated toxic gases and corrosive vapors that pose a threat to personnel and electronic systems. In this time of budget constraints, the military needs to find economical, as well as reliable devices to detect and quantify toxic gases. Chemical sensors will have widespread applications in the military, such as detecting chemical-warfare nerve agents, monitoring emissions from point sources, such as air strippers and coke ovens, and monitoring the concentrations of corrosive vapors around aircraft maintenance centers.

II. SOLID-STATE CHEMICAL SENSORS

Solid-state chemical sensors are projected to be a promising technology for detecting toxic gas species [1]. These devices have several potential advantages compared to the "traditional" technologies employed for gas detection and quantification. Two of the traditional technologies include gas chromatography (GC) and mass spectrometry (MS) [2]. Compared to these technologies, solid-state chemical sensors are less expensive, smaller, and simpler to operate.

Significant attention has been focused on the development of compact and inexpensive gas-sensing devices which possess a high degree of sensitivity, selectivity, and reliability. A variety of chemical sensors have been developed over the past decade that use microelectronics as the fundamental technology. A major feature of these devices is that they incorporate a chemically-sensitive polymer or metal oxide to detect the organic and inorganic gaseous compounds of interest, and to transduce the presence of the chemical moiety into a useful electronic signal [3,4]. The chemical polymers and metal oxides have been used with thick- and thin-film morphologies. At least six devices that incorporate chemically-sensitive films have been successfully used to detect nitrogen dioxide and some organophosphorus compounds [3,5,6]. The chemically-sensitive devices that have been developed

include: piezoelectric sensors [3,7], surface acoustic wave (SAW) detectors [8], chemiresistors [9,10], notch filters [11], the charge-flow transistor (CFT) [12], and the interdigitated gate electrode field-effect transistor (IGEFET) [12]-[16]. At the present time, the SAW device is considered to be the most advanced technology for solid-state gas detection. The chemiresistor, the notch filter, and the CFT have motivated the development of the IGEFET and CHEMFET.

III. CHEMFET CONCEPT

The chemically-sensitive field-effect transistor (CHEMFET) has the potential for detecting minute concentrations of gaseous compounds. The CHEMFET is a conventional metal-oxide-semiconductor field-effect transistor (MOSFET) which has an interdigitated gate electrode (IGE) structure, compared to a conventional solid metal gate contact, as shown in Fig. 1. The MOSFET and IGE structure are physically isolated. The IGE structure consists of a driven gate electrode and a floating gate electrode. A chemically-sensitive film deposited over these two electrode structures electrically couples the system. A detailed description of the CHEMFET design, fabrication, and operation is given in reference [17].

The chemical state of the thin-film IGE coating in the presence of a detectable gas or vapor determines its electrical conductivity, which is subsequently transduced as a change in the MOSFET's response. If the driven gate electrode of the IGE structure is excited with a pulsed voltage, it will produce a corresponding response characteristic in the drain current of the MOSFET. Thus, the changes in the gas-sensitive thin-film's electrical impedance can be detected via the corresponding changes in the drain current of the CHEMFET.

IV. EXPERIMENTAL APPROACH

The CHEMFET is fabricated by coating the IGE structure with a chemically-sensitive metal-doped phthalocyanine (MPc) thin film. Two film materials were used in this research effort: copper phthalocyanine (CuPc) and lead phthalocyanine (PbPc). These materials chemically react with the challenge gases, which represent the toxic or corrosive vapors that need to be detected. The challenge gas adsorbs onto activation sites on the surface of the MPc thin-film with a charge-transfer bond. This causes a net change in the number of charge carriers in the film, which correspondingly changes its electrical conductivity. The gases that were screened in this re-

search included: nitrogen dioxide (NO_2), dimethyl methylphosphonate ($C_3H_9PO_3$), boron trifluoride (BF_3), methanol (CH_3OH), carbon monoxide (CO), vinyl chloride (CH_2CHCl), and trichloroethylene (C_2HCl_3).

A gas generation and delivery system, shown in Fig. 2, was used to generate, control, and transport small concentrations of the challenge gases to the test chamber containing the CHEMFET microsensor [17]. Pressurized laboratory air was supplied to the gas-delivery system as the carrier and diluent gas. The air was passed through an activated charcoal filter to remove any organic contaminants. The filtered air was also passed through silica-gel beads to remove moisture, and thus, regulate the relative humidity of the challenge gas generation and delivery system. The humidity level was precisely controlled by passing the carrier gas through a deionized water bubbler, and the monitoring function was accomplished with an in-line hygrometer. Depending upon the gas delivery requirements, the carrier gas was passed to the challenge gas path or to the purge path. The flow of the carrier gas and the challenge gases were controlled with a series of mass flow controllers and permeation tubes. The use of mass-flow controllers in conjunction with the permeation tubes resulted in establishing precise concentrations of the challenge gases delivered to the sensor positioned in the test chamber. The internal temperature of the test chamber was regulated with an external power source and a regulator [17].

The CHEMFET was constructed by the Metal Oxide Semiconductor Implementation Service (MOSIS) (University of Southern California).

MOSIS fabricated the CHEMFET microsensor using the scalable 2-micron, double-metal, double-poly silicon, p-well technology. The IGE structure was fabricated with a second-level metal (aluminum), while a first-level metal was used to form the ground plane [12]. The CHEMFET IC die was configured as a symmetric array of nine, independently-operated sensors, and it was mounted in a 64-pin dual-in-line package (DIP), as shown in Fig. 3. Each IGEFET is integrated with its own impedance-matching differential input amplifier which consists of serially-connected MOSFET inverters. The amplifier section for each individual IGEFET reduces the complexity of the IC die analog signal paths. An independent MOSFET amplifier was incorporated in the IC die 64-pin package for the purpose of providing temperature compensation. To minimize electrical coupling in the CHEMFET microsensor, the driven-gate bond

pads were isolated from the floating-gate bond pads, and the amplifier input bond pads were isolated from the amplifier output bond pads.

Several different electrical measurements were conducted during this investigation. The IGE structure's dc resistance, and its ac impedance, as well as the sensor's frequency- and time-domain responses, were characterized. The electronic measuring instrumentation which was used to generate the required data included: an electrometer, impedance analyzer, gain/phase analyzer, spectrum analyzer, and a digital storage oscilloscope. The gas delivery system and the data collection instruments were controlled with a personal computer [17].

V. DEFINITIONS

The CHEMFET's sensitivity, selectivity, and reversibility can be defined in terms of its measurable parameters. The measurable response parameters include: the gain and phase of the device, the electrical impedance of the IGE, the direct current resistance of the IGE, and the microsensor's voltage-pulse response in the time- and frequency-domains.

The mean value of each measurable response parameter discussed above can be used to describe the CHEMFET's behavior (i.e., sensitivity, selectivity, and reversibility) for a specific set of physical operating conditions (i.e., thin-film type, thin-film thickness, temperature, challenge gas, and challenge gas concentration). Equation (1) yields the mean value, x , of a particular measured parameter, p , for a specific set of data:

$$x(p) = \left(\frac{1}{N}\right) \sum_{i=1}^N p_i \quad (1)$$

where N is the number of data points, and p_i is a discrete measured parameter. Using the mean values of the measurable parameters, a comparison can be made between the challenge gas produced values and the baseline values, so that CHEMFET's relative sensitivity, selectivity, and reversibility can be ascertained.

a) Sensitivity

The sensitivity of the CHEMFET is a measure of the lowest concentration of a challenge gas (*ch.gas*) that can be detected [13]. The sensitivity can be calculated with respect to the mean *baseline* response of the sensor (exposure to room air) relative to its response to a particular challenge gas concentration. Equation (2) formulates the normalized sensitivity of

the CHEMFET operating under a fixed set of physical operating conditions:

$$\text{Sensitivity}_{x(p)} = \left| \frac{x_{\text{baseline}} - x_{\text{ch.gas}}}{x_{\text{baseline}}} \right| \quad (2)$$

b) Selectivity

Selectivity is a measure of the CHEMFET's ability to distinguish among various challenge gases [18]. The selectivity of the CHEMFET can be determined by comparing the measurable parameters for each challenge gas. Equation (3) describes the selectivity of the CHEMFET for a particular challenge gas (b) relative to another challenge gas (a) with the same concentration:

$$\text{Selectivity}_{x(p)} = \left| \frac{x_{\text{ch.gas}(a)} - x_{\text{ch.gas}(b)}}{x_{\text{ch.gas}(a)}} \right| \quad (3)$$

c) Reversibility

The reversibility parameter describes the sensor's ability to return to its initial state after it has been exposed to a particular challenge gas. The reversibility performance of the CHEMFET is quantified with respect to time. For this relative measure, the challenge gas type is the same, but the concentration is varied. This relationship is given by Equation (4) [17]:

$$\text{Reversibility}_{\text{gas}} = \frac{x_1(c_1, t_1) - x_2(c_2, t_2)}{x_3(c_1, t_3) - x_2(c_2, t_2)} \quad (4)$$

where c_1 is the initial concentration of the challenge gas, and c_2 is the concentration of the challenge gas "plug". The points in time when the measurements are collected are represented by t_1 , t_2 , and t_3 . Time t_1 and t_3 represent the purge cycle for the CHEMFET, and t_2 corresponds to the instant of time during the exposure portion of the challenge gas cycle when the sensor manifests a saturated response.

VI. RESULTS

Preliminary tests were performed to establish a baseline response of the system from which a comparison could be made with the subsequent challenge gas exposure trials. One of the primary interests of this research effort was to investigate what effects the exposure time had on the performance characteristics (specifically, the reversibility) of the CHEMFET.

Establishing the carrier and diluent gas (filtered room air with a relative humidity (RH) of 2%) pre-exposure and purge duration cycles with respect to

the activation of the instrumentation was of primary importance. For one hour prior to the data collection process, the test chamber and the sensor packages were heated to the desired operating temperature, while the carrier and diluent gas was allowed to flow through the test chamber at a rate of 100 ml/min. After this initial period of achieving a stabilized temperature and sensor baseline response, the data collection process was initiated. After a period of fifteen minutes, a challenge gas "plug" was introduced into the test cell (see Fig. 4). The gas "plug" was a pulse of the challenge gas having a "width" of three minutes (the amount of time needed for the instrumentation to assay all nine independent sensing elements of the microsensor), and an "amplitude" corresponding to that of the desired concentration. After exposure to the challenge gas "plug", the CHEMFET was purged with room air at 100 ml/min until equilibrium (reversibility to within 90% of the baseline response) was achieved.

The physical operating parameters were investigated over a wide range. The thicknesses and types of the chemically active films were varied. The deposited thicknesses for the CuPc films were 250Å, 550Å, and 1000Å, whereas the thicknesses for PbPc were 300Å, 650Å, and 1100Å. The gases used to challenge the thin-films consisted of primary and secondary gases. The primary gases were NO_2 , $\text{C}_3\text{H}_9\text{PO}_3$, and BF_3 . The secondary gases were used for screening purposes only, and they consisted of CH_3OH , CO , CH_2CHCl , and C_2HCl_3 . The challenge gas concentrations ranged from as little as 10 ppb for some gases, and up to 50 ppm for other gases. Precise concentrations over a specified period of time were delivered via the mass flow controllers. The operating temperatures for investigating the responses to the primary challenge gases were set at 22°C and 110°C. For the secondary challenge gases, only one temperature setting of 70°C was used.

Since the purpose of this investigation was to evaluate the sensitivity, selectivity, and reversibility of the CHEMFET, the physical operating parameters were identified which produced the most significant sensitivity, the most significant selectivity, and the most complete degree of reversibility relative to time. The measurable response parameters produced by the CHEMFET included: the dc resistance of the IGE structure, the electrical impedance of the IGE structure, the gain and phase angle of the device, and the CHEMFET's voltage-pulse (time-domain) and normalized frequency-domain difference responses.

The most valuable measurements in this investi-

gation were the dc resistance and the sensor's gain. These two measurement parameters provided the most distinctive changes and characteristic responses to the challenge gas exposures. These measurements were used to compute the sensitivity and reversibility of the CHEMFET relative to the physical operating parameters. Figures 5 and 6 depict typical IGE dc resistance and device gain responses for a 1000 Å thick CuPc film exposed to NO_2 at 22°C [17]. The representative changes in dc resistance and device gain for various operating conditions of a CuPc coated CHEMFET are shown in Figs. 7 and 8 [17]. Determining the CHEMFET's selectivity for binary challenge gas exposures could not have been accomplished without the normalized frequency-domain difference responses [17]. Figure 9 illustrates a typical CHEMFET frequency-domain response to a 2.5-volt, 5 μ s duration excitation pulse applied to the driven-electrode contact (see Fig. 1) [17].

The smallest concentrations of the challenge gases that were detectable for both film types are shown in Table 1 [17]. The two exceptions are BF_3 and CO . BF_3 was only detected with the CuPc films, and CO was only detected with the PbPc films.

Of the metal-doped phthalocyanine thin-films investigated, CuPc was found to be the most sensitive (produced the largest changes in device gain) for detecting $C_3H_9PO_3$ and BF_3 . PbPc was found to be the most sensitive to NO_2 , CH_3OH , CO , CH_2CHCl , and C_2HCl_3 . For both film types, the sensitivity increased as the thickness of the films increased. In all cases the sensitivity decreased as the operating temperature increased.

The selectivity of CuPc and PbPc for the binary challenge gas mixtures revealed that the CHEMFET has the ability to detect two gases simultaneously. Even though the responses predominantly indicate the presence of the gas which generally manifests stronger response, the computation of the selectivity revealed that a second gas (with equal concentration relative to that of the more strongly reacting gas) can be detected.

All challenge gas exposures for both film types and their respective thicknesses were reversible at both operating temperatures. To determine the most complete degree of reversibility, the length of time to reach 90% of the CHEMFET's pre-exposed state was used. The challenge gas exposures less than 3 minutes in duration did not achieve a steady-state response during the time of exposure. The time required for full reversibility increased with increasing challenge gas concentration, exposure duration, and film thick-

ness. At higher operating temperatures, reversibility improved; however, the sensitivity and selectivity responses diminished.

VII. SUMMARY

The combination of microelectronics and organic chemistry affords a unique opportunity to develop simple and rugged, yet sensitive and selective chemical sensors. The CHEMFET design described in this work utilizes metal-doped phthalocyanine films (CuPc and PbPc) as the chemically-sensitive component of the gas sensor. The gases used to challenge the chemically-sensitive thin-films consisted of primary and secondary gases. The primary gases were NO_2 , $C_3H_9PO_3$, and BF_3 . The secondary gases were used for screening purposes only, and they consisted of CH_3OH , CO , CH_2CHCl , and C_2HCl_3 . The challenge gas concentrations spanned 10 ppb to 50 ppm. It was shown that the CHEMFET sensor is capable of detecting and discriminating trace amounts of gases that may pose an environmental hazard.

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Fig. 1. Interdigitated gate electrode CHEMFET. Legend: (1) chemically-sensitive thin film, (2) driven-electrode conductor, (3) floating-electrode conductor, (4) MOSFET drain contact, (5) MOSFET gate and floating-electrode contact, (6) MOSFET source contact, (7) driven-electrode contact, (8) MOSFET source region, (9) MOSFET drain region, (10) MOSFET drain-to-source channel, (11) host silicon substrate.

Fig. 2. Gas generation and delivery system.

Fig. 3. Optical photograph of the CHEMFET microsensor. The width of the IC die package window is approximately 0.5 inch.

Fig. 4. Challenge gas "plug" illustrating gas concentration with respect to duration of exposure.

Fig. 5. IGE dc resistance versus time for a 1000 Å thick CuPc film when exposed to a 1 ppm concentration plug of NO_2 at 22°C.

Fig. 6. CHEMFET gain response for a 1000 Å thick CuPc film when exposed to a 10 ppb and 1 ppm concentration plug of NO_2 at 22°C.

Fig. 7. Change in dc resistance of IGE structures coated with CuPc when exposed to NO_2 .

Fig. 8. Change in gain at 10 Hz of a CuPc-coated CHEMFET when exposed to NO_2 .

Fig. 9. CHEMFET frequency-domain response for a 1000 Å thick CuPc film when exposed to NO_2 .

Table 1. Lowest Detectable Concentrations of the Challenge Gases.

Challenge Gas	Lowest Detectable Concentration	Thin-Film Type
NO_2	10 ppb / 10 ppb	CuPc / PbPc
$C_2H_5PO_3$	50 ppb / 500 ppb	CuPc / PbPc
BF_3	10 ppm / *	CuPc / PbPc
CH_3OH	1 ppm / 1 ppm	CuPc / PbPc
CO	* / 10 ppm	CuPc / PbPc
CH_3CHCl	30 ppb / 30 ppb	CuPc / PbPc
C_2HCl_3	10 ppb / 10 ppb	CuPc / PbPc

* Not detectable