Sensors & Transducers

Field Effect Devices Sensitive to CO at Room Temperature

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Abstract: [5,10,15-Tris(2,6-dichlorophenyl)corrolate] cobalt(III) was used to chemisorb CO selectively, on the gap-gate of MOS capacitors and the state of charge monitored by voltage shifts of the photocurrent induced by pulsed illumination under constant D. C. bias, proportionally to CO concentration in air. Negative chemically induced charges at room temperature induce positive responses above and negative shifts below the threshold voltage, conforming to acceptor behavior, and the dynamic range (125 ppm) is limited by the silicon doping concentration. The linear proportionality between CO concentration and surface charge ($6.46[ppm.m^2.\mu C^{-1}]$) corresponds to the low concentration limit of the Langmuir isotherm. Sluggish CO desorption can be compensated by photo stimulation at 395 nm. *Copyright © 2014 IFSA Publishing, S. L.*

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1. Introduction

Carbon monoxide is toxic, because its affinity for hemoglobin is more than 200 times that of oxygen, resulting in the formation of carboxyhemoglobin, with even relatively low amounts of inhaled carbon monoxide, under extended exposure [1]. This sluggish release of CO from the active heme group (Fig. 1a) discourages its possible use as a sensing probe, whereas cobalt (III) corroles (Fig. 1b) have shown strong reversible chemisorption of CO [2], even in the presence of O_2 and N_2, due to increased electron density of the central metal. Two alternative strategies are possible to take advantage of the high resulting selectivity for their potential use in gas sensors [3]: either functionalize these compounds [4] to obtain continuous thin films suitable for conductimetric probes, or resort to sensing techniques independent of compound resistivity or state of aggregation, such as SAW [5-7].
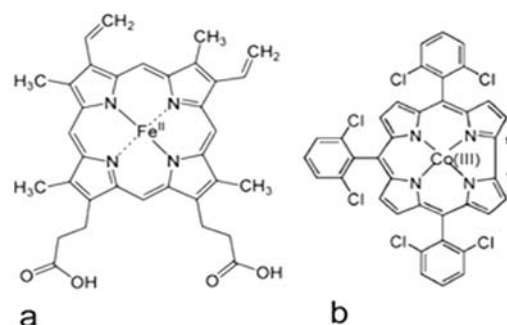

Fig. 1. Heme and Co-corrole structures. a) Heme B, b) 5,10,15-Tris(2,6-dichlorophenyl)corrolate] cobalt(III).

FET devices have been employed with organometallic sensing films at room temperature in a conductimetric mode [8], which monitors compound resistivity changes in response to chemical stimulation at very low concentration (<15 ppm), whereas gap-gate devices interrogated by pulsed illumination techniques extend the dynamic range beyond 100 ppm [9]. This work addresses the application of the latter method to CO detection, at room temperature, with Co-corrole active films.

2. Materials and Methods

Gap-gate MOS capacitors [9] were fabricated with 4-40 Ω.cm, p-type, boron doped silicon wafers, thermally oxidized to 130 nm. Circular (2.5 mm O. D.) magnetron sputtered chromium gates were masked, leaving a 250 micron gap, to allow the inversion layer to extend continuously beneath it under positive polarization (Fig. 2), thus relieving the chemically sensitive material of any electrical functionality. The capacitors were mounted on hybrid alumina substrates and enclosed in an air tight chamber, for pulsed illumination measurements [10], with previously described instrumentation [11]. All devices were cycled repeatedly, biased from deep-inversion to depletion, until reproducible dependence of the photocurrent (u) with bias voltage (V_A) was verified.
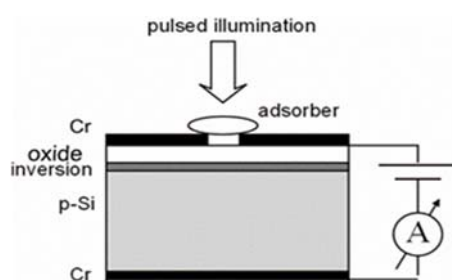
Fig. 2. Schematic sensor cross section, represented under forward applied bias, which induces a continuous inversion layer across the gap of the gate electrode, over which a Co-corrole dichloromethane solution is seeded, for detection by the phase sensitive amperometric circuit.

A KEITHLEY Source and Measure Model 2400 unit supplied constant applied bias, and allowed monitoring of the polarization current. Pulsed illumination with a HITACHI HL6501MG, 658 nm, 35 mW laser diode, thermally stabilized and driven by a THORLABS LTC-100-B unit, modulated at 1 kHz, induced a photocurrent (u), which was monitored phase sensitively with the HL6501 photodiode reference, on a SIGNAL RECOVERY Model 1265 lock-in amplifier operated in external mode, after pre-amplification by an ad-hoc transimpedance current to voltage converter [11], through calibrated 10 kΩ load resistors and the respective signals were displayed on a Tektronix TDS 220 dual channel oscilloscope. Constant flow of synthetic air and 1000 ppm CO in N_2

gas mixtures, totaling 100 cm^3/min, was secured with independent MKS 1259 mass flow controllers.

5,10,15-Tris[(2,6-dichlorophenyl)corrolate] cobalt(III), synthesized at DQIAQF-UBA by previously described methods [12], yielded UV-Vis and 1H NMR spectra coincident with those reported in [4]. 20 μL of a 10^{-3} molar solution of this compound in dichloromethane were delivered directly to the gap window, with a micropipette, before each measurement. Consistently with prior reports [8], it was found beneficial to expose the device to 50 ppm CO in nitrogen or air carrier to activate the corrole deposit. Although long term exposure to light and air is known to induce oligomerization [13] in analogue Co-corroles, no perceptible CO sensitivity changes were found, for dichloromethane solutions stored in caramel bottles, even after three months.

3. Results and Discussion

The response to chemical stimulation by mass flow controlled mixtures of 100 ppm CO, in nitrogen or dry-air indistinctly, with a constant 100 cm^3/min total flow, defined by the shift in bias tension at constant photocurrent, is negative in the depletion regime below the threshold voltage (V_T = 2.5 V, Fig. 3a) and positive under full inversion above this limit (Fig. 3b), consistently with an acceptor character, associated with negatively charged chemisorbed species [14].
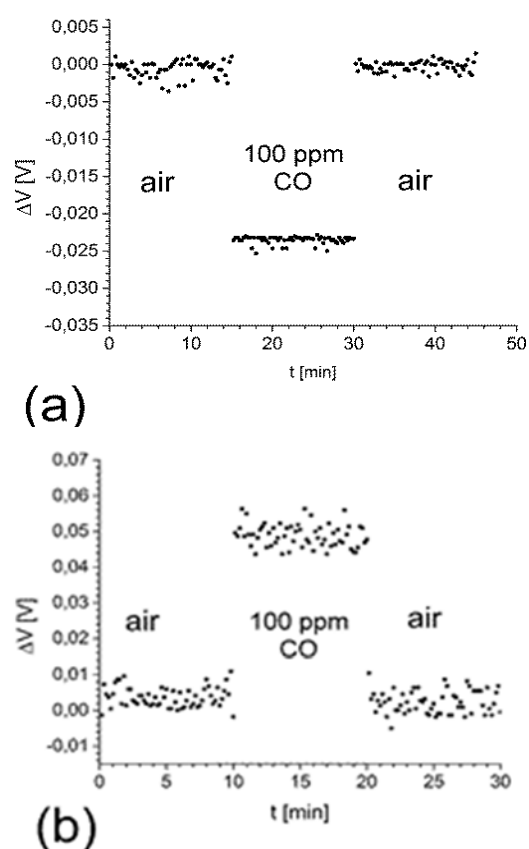
Fig. 3. Temporal dependence of responses to 100 ppm CO in air, 20 °C (a) biased at 2.2 V < V_T; (b) 3.5 V > V_T.

Room temperature operation narrows the difference between threshold and flat band voltages, rendering the photocurrent voltage dependence steeper [15], such that if device geometry is increased to allow for inverse response in the depletion mode, the normal response in full inversion mode exceeds the dynamic range of the detection circuitry.

A representative example of the temporal response to increasing CO stimulation in dry air, at 20 °C, monitored in full inversion, under 3.9 V polarization, is illustrated in Fig. 4.
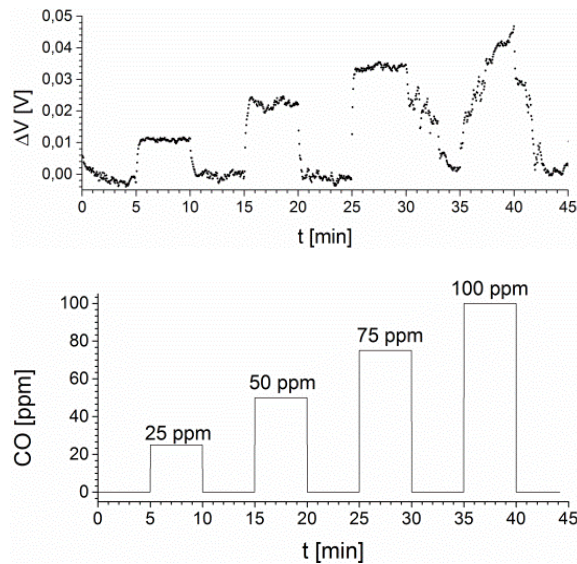

Fig. 4. Temporal response to increasing 5 minute CO stimulation in air, at 20 °C, biased at 3.9 V, illustrating the influence incomplete CO desorption.

Initial response and relaxation are commensurate with the sampling interval (3 s), consistently with fast charge transfer processes, but the third stimulation at 75 ppm displays a relaxation transient, disclosing a kinetic barrier for CO desorption, which subsequently hampers adsorption as well, in the fourth stimulation at 100 ppm. Upon further chemical stimulation (Fig. 5), no return to base line is observed and ultimately, sensitivity is lost, unless CO desorption is stimulated, either thermally or by cycling in vacuum [7].

Since capacitors are charge transducers, the strong dependence of the measured ΔV response on operating conditions may be eliminated by computation of the chemically induced charge, through the product of the high frequency capacitance at the bias of interest and ΔV, to obtain a surface charge density uniquely dependent on stimulus concentration [15] (Fig. 6).

The dynamic range of these devices is limited by the maximum sustainable charge at the dielectric interface, which is a function of the doping level of the semiconductor ($N_A^{2/3}$) [16], corresponding to 23.5 $\mu C/m^2$ for the wafers employed in this work; consequently, only the low concentration regime of

the Langmuir adsorption isotherm is accessible for measurement, which yields the linear dependence of surface charge on concentration apparent in Fig. 6.
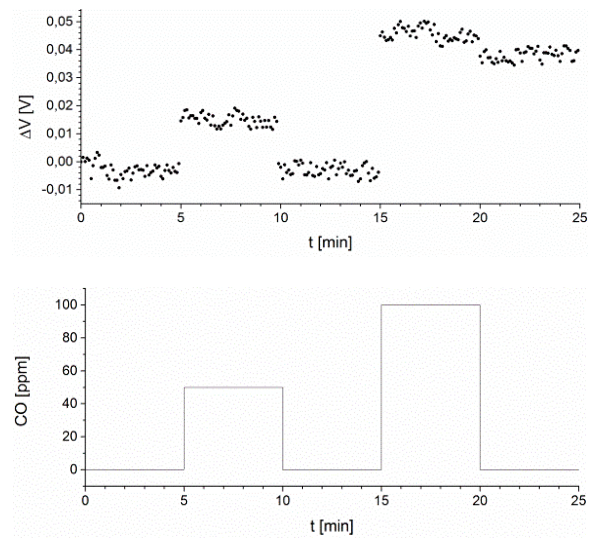
**Fig. 5.** Response relaxation from 100 ppm stimulus is inhibited by un-desorbed CO ($V_{bias} = 7.0$ V).
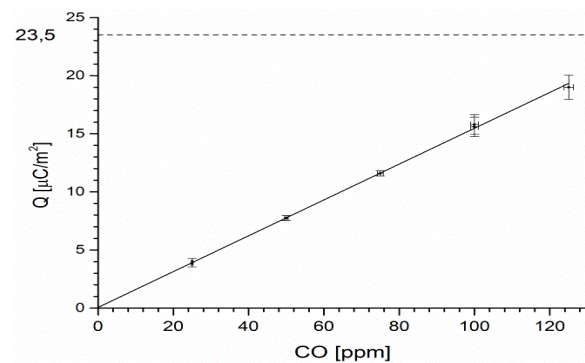
Fig. 6. Chemically induced surface charge as a function of CO concentration in air (6.46[ppm.m^2.μC^{-1}]) (full line), at 20 °C, and the upper limit of the dynamic range (dashed line), corresponding to $N_A^{2/3} = 23.5$ μC/m^2, for 4 Ohm.cm boron doped wafers. Error bars are standard deviations of 100 measurements.

The sensitivity slope of the fitted straight line (6.46[ppm.m^2.μC^{-1}]) corresponds to the product of the chemisorbed complex ionic surface charge and the Langmuir equilibrium constant.

Whenever a common mechanism mediates the chemisorption of different analytes, interference cannot be avoided. Such is the case of NO_2 and SO_2 on gold, where sensitivity doubles for the latter, consistently with doubly charged chemisorbed species, thus halving the effective dynamic range [11, 17]. At higher concentrations, in the case of donor stimuli, such as hydrogen on Pd or Pt gates, the excess positive charge is swept to ground and maintained at the maximum, consistently with electrical saturation, whereas with acceptor stimuli, the negative

chemically induced charge is completely drained by forward bias, yielding an apparent null response [11].

The CO pressure for half occupancy of the Co-corrole adsorption sites, measured by gas uptake [2], yields a very low 0.37 torr, compared to an oxygen equivalent of 946 torr, with a ratio of 2557, which is evidence for highly selective chemisorption of CO and chemical saturation, at almost 500 ppm, well in excess of the electrical capacitive limit. This high affinity for CO hampers its ready release after repeated stimulation, consistently with prior reports [7] in which vacuum was used to promote desorption. Heating to 80ºC, in 1 atm of air, can likewise restore the initial base line but the ensuing delay to stabilize the measurement disrupts continuous operation. Photodesorption provides a convenient alternative. Continuous illumination at 395 nm, coincident with the B band of Co-corrole (Fig. 7), with an EPITEX L395-06 LED, rated at 3.0 mW total radiated power, over 9º solid angle, operated at 20 mA, for one hour, is sufficient to restore sensitivity. The B or Soret absorption band corresponds to a spin allowed triplet $(S = 1)$ to quintuplet transition $(S = 2)$, by contrast with the spin forbidden Q band [18]. DFT calculations [19] show that the electron configuration of the quintuplet state, $(dxy)^2 (dz^2)^2 (d\pi1)^1 (d\pi2)^1 (\phi cor')^1 (\phi cor)^1$ for S=2, results from excitation of a filled bonding corrole orbital $(\phi cor')$, to an unfilled corrole orbital (ϕcor) of antibonding character, associated with an extension of the C9-C12 bond (Fig. 1b). Hence, comparatively modest constant illumination intensities, which do not interfere with the pulsed illumination at 658 nm, are sufficient to promote CO desorption.
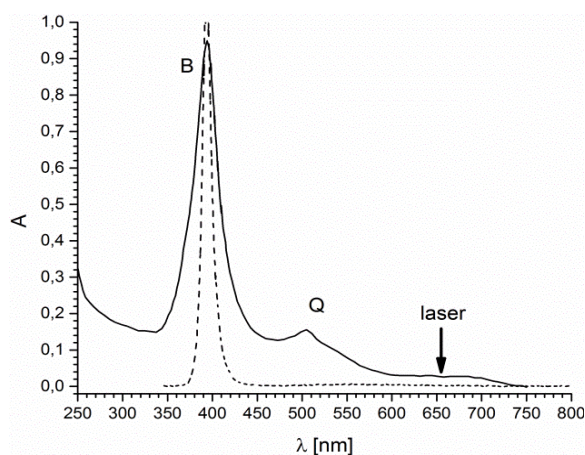
Fig. 7. Absorption spectrum of a [5,10,15-Tris(2,6-dichlorophenyl)corrolate] cobalt(III) in dichloromethane (full line) displaying the B and Q bands, superposed on the normalized emission spectrum (dashed line) of the EPITEX L395-06 LED used for photodesorption. The arrow indicates the wavelength of the HITACHI HL6501MG laser used for pulsed illumination, beyond the corrole absorption range.

The early work on chemically sensitive field effect devices [20] was dominated by metallic chemisorbers,

such as Pd, Pt, Au and their alloys, in which comparatively low adsorption enthalpies (≈20 kCal/mol) favored chemical saturation of available adsorption sites, which required high operating temperature (≈150ºC) to release their occupancy, albeit much lower than semiconducting conductimetric alternatives. It has become apparent [21] that organic and organometallic compounds can overcome this limitation, particularly if additional requirements such as favorable electrical properties can be avoided. Field effect devices are suitable, whenever chemisorption is associated with the formation of an electrically charged chemisorbed complex.

Cobalt corroles configure planar molecules [22], with 4-fold coordinated Co(III), for which changes in oxidation state are unlikely, due to lack of flexibility to accommodate the ensuing ionic radii changes, consistently with electronic structure computations [19]. Nonetheless, their redox cycles confirm one electron oxidation [23], unassociated to the central cation, which preserves its gyromagnetic factor under ESR monitoring, thus confining charge transfer to the macrocycle.

4. Conclusions

The chemisorption of CO on 5,10,15-[Tris(2,6-dichlorophenyl)corrolate] cobalt(III) yields a negatively charged complex, which renders detection by field effect devices possible at room temperature. Based on its oxidation behavior [23], it can be inferred that the pertinent charge transfer is located on the macrocycle, rather than the central metal. Only the low concentration limit of the pertinent Langmuir adsorption isotherm is accessible for measurement, because the dynamic range is limited by the two thirds power law on silicon doping concentration [16], which restricts the maximum accumulated charge. The high affinity of the corrole for CO, which promotes selective sensitivity, can also hamper desorption, which can be conveniently photo stimulated by illumination at 395 nm.

Acknowledgements

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