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# Integrated Sensor For Gas Detection Based On Phtalocyanines Derivatives

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*Abstract:* - The paper presents the layout and the technological steps for an interdigitally integrated capacitor used for gases detection. Silicon micromachining technology is applied for manufacturing the sensor substrate. The sensitive layer used is phthalocyanine (Pc) deposed by EDL (evaporated dyes layers technique). Many solutions were found as phthalocyanine derivatives deposition technique. Considering the different sensitivities of phthalocyanines derivatives, we obtained different gas sensors. The copper phthalocyanine (Cu Pc) and nickel phthalocyanine (Ni Pc) have been investigated for $NO_x$ detection. The measurement of sensors for $NO_x$ and $NH_3$ detection will be presented as concentration versus impedance.
The microsensors testing structures deposited with phthalocyanines were investigated by impedance measurements in a vacuum chamber controlled by a gas analyzer.
The measurements were made at room temperature but a medium temperature is applied (<200$^0$C) after measurement, for cleaning the material in order to reuse the sensor. The sensor is integrated, MOS compatible, cheap, easy to be used and has a low power consumption.

*Key-Words:* - sensors, gas detection, chemisorption, phtalocyanine, conductivity, micromachines, polysilicon

## 1 Introduction

The gas sensors are commonly used for pollution control measuring low concentrations of pollutant gases in air, generated by motor vehicle or industrial emissions.

The main factor to be considered in selection of NO, $NO_x$, or $NO_2$ sensors for measurements in ambient environments or in biomedical field is the sensitivity.

Nitrogen dioxide ($NO_2$), nitrogen monoxide (NO) and carbon monoxide (CO) represent a significant health hazard for every one of us; the first alarm threshold limit is set at concentration of 200 $\mu g/m^3$ (106 ppb) for $NO_2$ and 15 $mg/m^3$ (13 ppm) for CO/1/.

The operating principle of the gas sensors is based on the change in conductivity due to the chemisorption of gas molecules at the sensitive layer surface. The integration of standard CMOS technology with conducting sensitive layer as phthalocyanine (Pc) deposited by EDL technique was one of the goal of our research. We deposited three types of layers phtalocyanine based: copper phthalocyanine (CuPc), nichel phthalocyanine (NiPc) or iron phthalocyanine (FePc) films to be used as gas sensitive layers for the detection of NOx, and $NO_2$ in ambient air.

The layout and the technological steps of a gas sensor based on an interdigitated capacitor integrated with a polysilicon heater, micromachined on a silicon membrane, CMOS compatible, and the test measurements for NOx and $NO_2$ are presented.

The microsensors deposited with phthalocyanines were investigated by impedance measurements in a vacuum box controlled by a gas analyzer. Small quantities of these gases can be detected by measuring the resistance of a Pc film. The gas sensors were tested in a box at a constant temperature and their resistance was determined function of $NO_x$ and $NO_2$ concentration and in presence of an inert gas $N_2$ . The integrated heating element consists of a polysilicon layer underneath the active area. A temperature sensitive resistor will enable precisely temperature control. The sensor is integrated in CMOS technology adding special micromachining processes.

It comes out that these sensors prove stability and sensitivity in polluted air.

## 2 Sensor Design And Fabrication

The schematic drawing of the sensor chip is presented in Fig.1. The scheme present the layout

and the cross – section of the sensor chip presenting information about technological steps and sensor design. The layout is a simplified version, the interdigitated electrodes having a higher number of fingers/2/. The real structure of the sensor will be presented by SEM pictures. The fabrication process starts with thermal oxidation of the silicon wafers and patterned before the selective ion implantation. High dose boron ($9 \cdot 10^{15}$ $cm^{-2}$, 100 KeV) is implanted and diffused followed by a boron doping from solid source + diffusion (1050°C, 4 hours). In this way it was realized the p-n junction, 12 μm depth, for anisotropical stop etch, in two steps, for obtaining the requested depth. After boron diffusion the thickness of the oxide grown on the silicon surface is $X_{ox}$ = 8000 Å. The masking layer for the anisotropic etching on the backside of the wafer and for isolation is obtained by the deposition and configuration of a 2000 Å $Si_3N_4$ layer. The next step is the deposition and the configuration of a 4000 Å boron doped polysilicon layer. After polysilicon

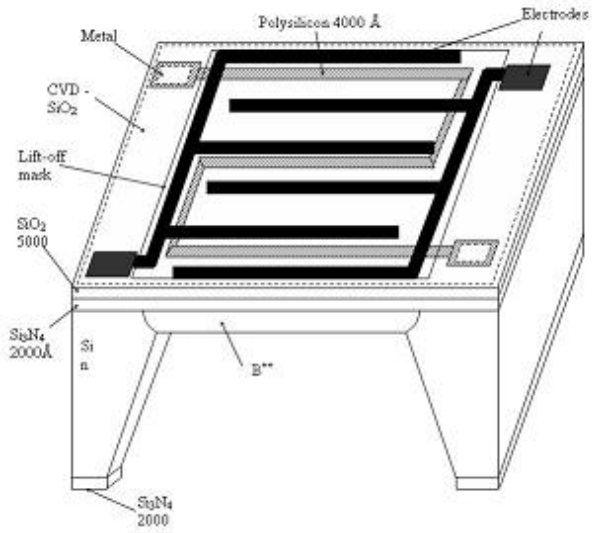


Fig.1. Scheme of the sensor chip

configuration, the resistor serving as heating element is obtained. A simplified version could be to use the silicon membrane high doped with boron as heater, without polysilicon resistor.

A CVD oxide is deposed such as dielectric layer and the contacts at polysilicon layer are open. Cr-Au deposition and configuration follow. Then the interdigitated electrodes, the resistor for monitoring the chip temperature and the necessary bond pads are defined by photolithography above the insulated heater element. The gold (Cr-Au) was used as electrode material to achieve a good contact with the Pc film. The utilisation of Al as electrode material give us, also, very good results.

The following step was the deposition and the configuration by double side alignment of 2 μm borophosphosilicate glass (BPSG), as mask material for the anisotropic etching, which has a low temperature deposition (<400 $^0$C) and can be used after metallization.

BPSG layer can be easily removed and the contact and the pad windows are opened. The etching is stopped at $B^{++}$ doped regions where the etching rate is very slow and the thickness of the membrane is also, defined. In the case of silicon anisotropic etching in EDP type F (ethylenediamine: pyrocathecol: water:1000ml:160ml:160ml), BPSG can be replaced by densified CVD/3/. The utilisation of BPSG, densified CVD as mask materials and

EDP as etching solution allow us to obtain the compatibility of the anisotropic etching with the I.C. technology.

Phthalocyanines films of various thickness (40nm for CuPc and NiPc; 20 nm for FePc) were vacuum evaporated onto the substrates of the interdigitated electrodes in order to analyse their sheet resistivities. The phthalocyanine film temperature could be very accurately controlled by the integrated heating element and thermoresistor. For an accurately deposition of Pcs in the active area of the device, the lift off technique will be used.

The SEM picture of the encapsulated sensor, covered with phthalocyanine is presented in Fig.2.

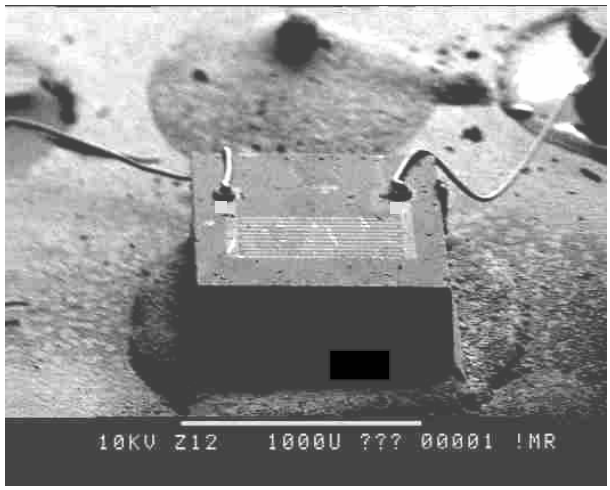


Fig 2. SEM picture of the sensor chip

The active area of the sensor contains the metal electrodes. The thickness of the metal layer (Cr-Au) is 400 nm. It is important to study the uniformity of the covering with Pc in order to prevent degradation by clustering of the contact metal.

On a substrate with electrodes on top, Pc film forms not a continuous film over the edge of the electrode strips because during the evaporation of the film the incident angle of the Pc molecules is not exactly normal to the substrate and on one side the strip edge forms a kind of shadow /4/. The film thickness at his point is probably smaller than the average thickness. The electrode strips are much higher that the Pc film deposited on top. We expect a relative bad covering of the strips and a

relative high number of cracks caused by the edges of capacitor strips. Pcs films deposited on electrodes had high resistance measurement values: 10 MΩ for CuPc, 15 MΩ for NiPc, 30 MΩ for FePc.

The cracks can be observed in Fig.3 and 4. For a better integrity of Pcs layer we will act for design and technology changes in order to obtain the planarization of the substrate.

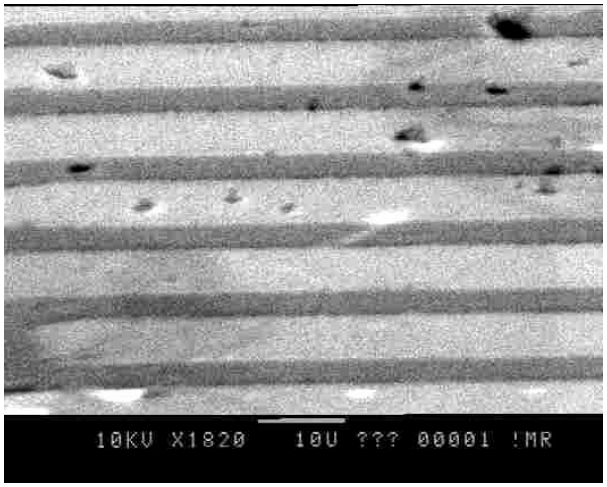


Fig.3. SEM picture of the electrodes covered with 40 nm CuPc area

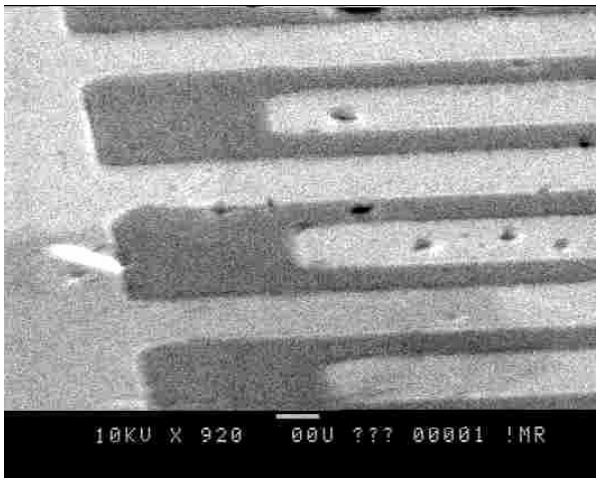


Fig.4. SEM picture of the electrodes covered with 20 nm FePc area

## 3 Experiments

Thin sensitive phthalocyanines films were deposed by evaporation /5/ to obtain gas sensors.

The sensors have been tested in a plexiglass box at a constant temperature and the resistance was determinated function of $NO_2$ and $NO_x$.

For the $NO_2$ analyse, 2ml of concentrated $HNO_3$ allowed to evaporate in a Petri dish inside the Plexiglas box and the responses were measured after every 20 seconds. The entire experiment was done in an automatic manner and the electronic circuit was entirely enclosed in a plexiglass box to avoid electrical interferences.

Sensitivity of NOx and $NO_2$ has been tested with a gas analyser; calibrations of each gas have been repeated at least 5 times, typical reproducibility of the sensor response were at 1-3mV.

The method used for Pc deposition was EDL, as evaporated Pcs at 200 ÷ 400 °C under high vacuum (~ $10^{-5}$Torr) forms a film of 40-50 nm for CuPc or NiPc and 20 nm for FePc onto the chip with interdigitated electrodes for conductance measurements. The thickness and the speed ($10^{-4}$ ÷ 1 nm/s) of deposition of the metal phthalocyanine film was controlled with a quartz balance.

It comes out that these metal phthalocyanines films are very stable and sensitive in very aggressive environments. The measurements were made at room temperature but a medium temperature is applied (< 200°C) after measurement, for cleaning the material in order to reuse the sensor; in our case the temperature applied was 150 °C for one hour.

The figure 5, 6 show the sensor characteristics for 40 nm CuPc film in $NO_2$ and NOx.

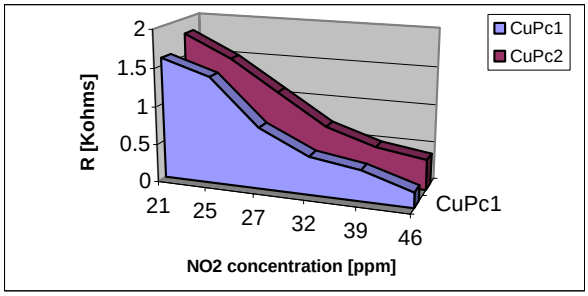


Fig.5. Resistance versus $NO_2$ concentration for CuPc

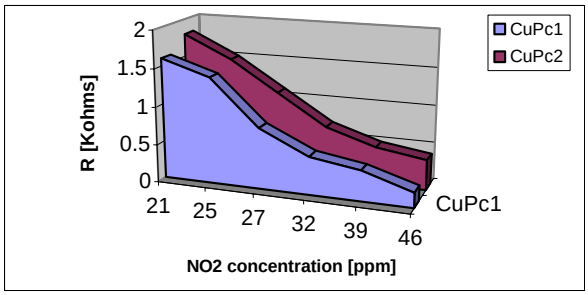


Fig.6. Resistance versus NOx concentration for CuPc

Metal phthalocyanines exhibit changes of conductance in presence of very small (ppb) concentration of oxidizing/reducing gases; their bulk conductance ranges from $10^{-6}$ to $10^{2}$ $ohm^{-1}$ $cm^{-1}$.

## 4 Results And Discussions

The measurements indicate us the decreasing of the resistance with the increasing of the concentration for $NO_2$ and $NO_x$ gases and for all types of phtalocyanines and sensors (Fig.5-10).

Two different area are used for sensors in order to study the sensitivity function of layout. Different read out values has been obtained, showing the influence of the sensors dimensions in response. The reproducibility of the silicon technology will allow us to obtain identical and reproducible sensors.

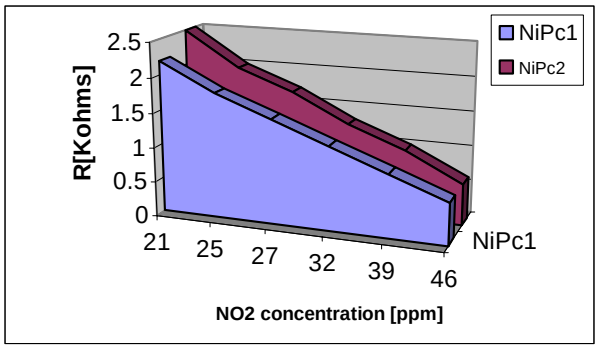


Fig.7. Resistance versus $NO_2$ concentration for NiPc

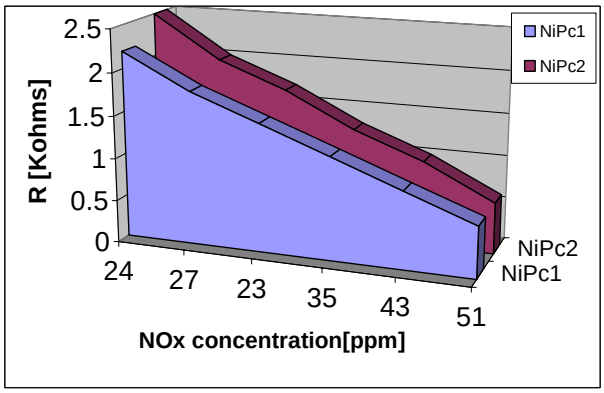


Fig.8. Resistance versus NOx concentration for NiPc

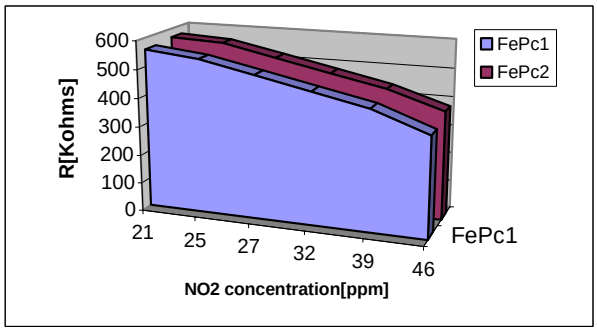


Fig.9. Resistance versus $NO_2$ concentration for FePc

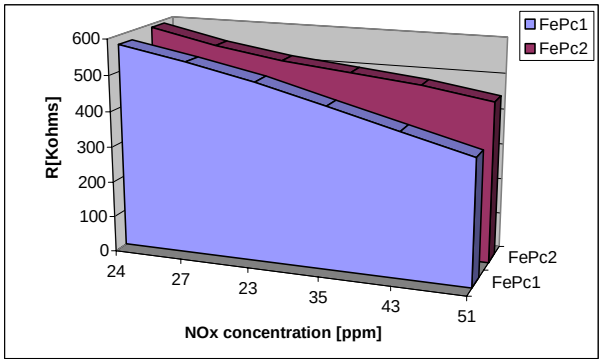


Fig.10. Resistance versus NOx concentration for FePc

Phthalocyanine structure is a large planar molecule with a delocalized electron system, which can easily be ionized. A phthalocyanine molecule is a good electron donor. The ring of N atoms around the central metal forms a potential well, which is responsible for the semiconducting properties. Metal phthalocyanines are very stable from chemical and thermal point of view, as a result of their intrinsic structural characteristics. The operating principle of the sensors is based on the change in conductivity due to the chemisorption of gas molecules at the semiconductor surface. Depending on whether the reaction is oxidizing or reducing, acceptors or donors will be produced at the film surface leading to the formation of a space-charge layer and modification of the free carrier density.

The differences in sensitivity for Cu, Ni, FePcs can be explained by the electronic configuration of metals coming in Pcs composition. The simple Pcs conductivity is usually low (approximately $10^{-14}\Omega^{-1}cm^{-1}$). The transitional metals help the conduction due to electron transport through redox system. The metal is much more efficient if it forms plan complexes with conjugate ligands (Pc). An excellent example is CuPc which has the highest mobility between of all organic compounds (75 $cm^2/v.s$). Here "$dz^{2"}$ orbitals of copper superpose with "3d" orbitals of azomethane of adjacent molecules with 0.388 nm interplanare distance.

When air alone was exposed to the Pc film, the signal change was insignificant compared with that on exposure of the air and nitrous oxide mixture. When the exposure time of gas was longer than 5 minutes, there was no further current increase recorded showing that the Pc film has been saturated.

## 5 Conclusions

Three main types of thin phthalocyanines films have been studied from point of view of NOx and $NO_2$ sensitivity: CuPc, NiPc, FePc. They exhibit changes of conductance in presence of small concentration of nitrogen oxides gases. Resistance measurements have been done without contact problems for Pcs films deposited on interdigitated electrodes

The sensitivity and stability of the sensor are sufficient for applications during the measurements made at room temperature of polluted air and even aggressive environments such as the $NO_2$ steams from $HNO_3$ 100%. The temperature of 150 °C was applied for one hour, for cleaning the material (metal phthalocyanines films) in order to reuse the sensor.

The sensor in entirely integrated, MOS compatible, cheap, easy to be used and has a low power consumption.

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