Ibernam 2009

Encuentro anual de la Red Española de Micro y Nano Sistemas

Sevilla, 26 y 27 de noviembre de 2009
IBERNAM 2009

Encuentro anual de la red española de micro y nano sistemas

26 y 27 de noviembre de 2009

Escuela Superior de Ingenieros
Universidad de Sevilla

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PRESENTACIÓN

La red **IBERNAM**, creada en 2001, tiene como objetivo prioritario la investigación y el desarrollo de microsistemas sensitivos muy avanzados mediante incorporación de nanoestructuras con el propósito de crear dispositivos cada vez más pequeños que aúnen inteligencia, fiabilidad, bajo consumo energético, portabilidad e intercomunicación inalámbrica.

Como es tradicional en el marco de nuestras actividades, este es el noveno encuentro entre los socios donde ponemos en común nuestros avances, resultados, y planeamos futuras colaboraciones que habitualmente se materializan en proyectos competitivos de carácter internacional y nacional. La experiencia de esta dinámica de convergencia de intereses y recursos ha mostrado ser eficaz a la hora de obtener resultados.

Este año 2009 se ha procedido a regularizar la situación administrativa de la red, cuyo origen fue el anterior Grupo Español de Sensores, que queda registrada con el nombre de **Red Española de Micro y Nano sistemas IBERNAM**. Asimismo se han renovado los cargos de la Junta Directiva para potenciar la actividad de la Asociación.

En el momento presente pertenecen a la misma 25 Grupos de investigación y desarrollo procedentes de los sectores Académicos, OPIS, Centros Tecnológicos y Grupos Industriales.

También quiero señalar que hemos hecho coincidir **IBERNAM 2009** con la reunión de la Plataforma Nacional Génesis en función de la gran afinidad que guardamos con ella y para ofrecer la visibilidad de nuestra red a la Administración y a los representantes de las plataformas europeas ENIAC y EPOSS.

Quiero agradecer vuestra presencia a todos los participantes, en especial a los conferenciantes y ponentes el esfuerzo en preparar las comunicaciones que nos enriquecerán a todos.

Este año el anfitrión es la Escuela Superior de Ingenieros de la Universidad de Sevilla quien nos acoge, y a quién agradezco su hospitalidad, en especial a los miembros del Departamento de Ingeniería Electrónica y al Comité local por la excelente organización.

F. Javier Gutiérrez Monreal
Presidente de IBERNAM
PROGRAMA

Jueves 26 de noviembre. Sala Juan Larrañeta

9:00-12:00 Asamblea Génesis

12:30-12:45 Inauguración Ibernam 2009

12:45-13:30 Sesión invitada "SiC-based sensors", por José Millán, CNM

13:30-14:30 Almuerzo

14:45-17:15 Presentaciones orales

17:30-19:00 Asamblea Ibernam

17:15-17:45 Presentación IEEE GOLD

20:00-21:00 Visita Real Alcázar de Sevilla

21:30- Cena. Restaurante "Los Seises".

Viernes 27 de noviembre. Sala Juan Larrañeta

9:00-9:45 Sesión invitada "Micro-nanotechnologies: An approach to develop In Vitro Diagnostic Devices", por Kepa Mayora, Ikerlan

10:00-12:00 Sesión póster. Planta Baja

11:00-11:15 Pausa café

12:15-13:00 Sesión invitada "GMR Current Sensors for IC applications", por Cándid Reig, Universidad de Valencia

13:15-13:45 Despedida

15:45-18:45 Visita Planta Solúcar Solar
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Fabrication of Metal Photonic Crystals from Macroporous Silicon

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Abstract—We describe the fabrication and results of simulation of metallic and metallo-dielectric Photonic Crystals (PhC) consisting in periodic 2D and 3D (modulated) arrays of Nickel. The fabrication process developed in this work allows to obtain both the direct structure of Nickel pillars, and the reciprocal structure of Inverse Opals in a Nickel background. The process starts by creating a Macroporous Silicon PhC that is used as a mold and if desired removed afterwards. To obtain the inverse structure, the pores of the silicon PhC are filled with Ni by electro-deposition. Otherwise, to recreate the original PhC, e.g. to obtain an array of inverse opals, the pores are first filled with polymer and eliminate the Si. Then Nickel electro-deposition is done. In this paper, we present the results of the fabrication of these PhC, and suggest some useful applications, such as new high-sensitivity sensors.

Keywords: Photonic Crystal, Metallo-dielectric Photonic Crystal, Macroporous Silicon, Electrodeposition.

I. INTRODUCTION

The initial description by Yablonovitch[1] of a Photonic Crystal (PhC), was one of a metallic structure that operated at microwave frequencies. The desire to achieve operating frequencies in the infrared (IR) and visible light, drove research to obtain smaller feature size. It was also proposed, [2] that PhC’s could be integrated in digital IC to fabricate compact and versatile devices, e.g. all-optical switches for optical communications, integrated waveguides or optical modulators. PhC’s are recent devices, and several techniques and materials have been proposed to fabricate them. [3][4] Nevertheless, the preferred materials used for their fabrication are dielectrics, either semiconductors (as Silicon or III-V compounds) or oxides (e.g. TiO), as one of the requirements to obtain a useful PhC is to use high contrast in the dielectric properties of the materials.

PhC’s are structured materials, with a regular dielectric spatial distribution, that show the property of creating photonic bandgaps in which light can not propagate inside the PhC, and is totally reflected. In its simplest form, PhC’s can be used to create perfect mirrors at a certain frequency range corresponding to a bandgap.

It is shown [2][5] that to create effective PhC’s, with large bandgaps, the dielectric distribution must define high contrast areas. Dielectrics or semiconductor materials have moderate refraction indexes, thus new compounds are searched with higher refraction indexes. Literature suggests that metals are a good choice, and several works try to create metallo-dielectric PhC’s (MDPC) able to work close to the visible region, [6] using complicated structures and processes. We propose a way to fabricate these structures that overcome many of these problems, and have built an effective MDPC in the mid-infrared (MIR) region.

II. FABRICATION

To obtain the Metallic PhC we: use a macroporous silicon (MpSi) template. MpSi can be fabricated with high precision and can be 3D modulated. The process starts with the fabrication of the MpSi PhC with an anisotropic electrochemical etching attack in hydrofluoric acid (HF); with this process we are able to obtain large arrays of ordered pores and very high aspect ratios. The basic process creates straight pores growing along the <100> axis of the Si crystal, thus creating a 2D PhC in a (100) oriented wafer. Furthermore, by modulation of the bias currents, we can create 3D PhC, as we modulate the pore profile in a sinusoidal-like curve. We have refined the etching process to obtain 3D PhC of the highest quality, least defects and minimal variation.

With this MpSi mould ready, we proceed to create the metallic structure. We propose two processes depending on the desired result:

A. Inverse (Negative) Structure

This structure is the reciprocal of the template, i.e. the obtained structure has the shape of the void parts of the original PhC. In this way we create pillars instead of pores, and for decreasing pore radius we can even get nanowires. This is the simplest of both techniques, as it only adds a fabrication step: nickel electro-deposition.

To make the electro-deposition we prepare a porous membrane from the MpSi PhC, with the pores open at both sides, by anisotropic etching in TMAH. The back-side is then covered with a thin film of evaporated copper to make the electric contact. The membrane is then immersed in an electrolytic bath with a nickel electrode. Nickel deposition
starts at the Cu interface and pore walls, and grows inside the pore. As an optional final step, we may choose to remove the remaining Si in HF to release the metallic structure.

B. Direct (Positive) Structure

This is somewhat a more complex process, as we need to make a template of the original PhC matrix. This is achieved by infiltrating it with a polymer. The fabrication has thus an extra step before electro-deposition. Once the membrane is ready and metallized, we pour PDMS on it and cure it. It is very important to eliminate any bubbles that may remain in the liquid polymer, and the pores. This is a necessary step to allow the liquid to infiltrate the MpSi, and completely fill them without defects. Once the polymer hardens, we eliminate the Si structure with an HF etch, thus we obtain the negative structure, as we did before for the nickel plating. The new PDMS mould is then used to create the original, positive, structure with the aforementioned electro-deposition process.

III. SIMULATION AND MEASURE

The theoretical study is needed for the design of the MDPC before its physical implementation. We are interested in studying the band structure and the optical behaviour of the metallic PhC to optimize it, and later fine tune the simulation system with actual measures with the FT-IR. This adjustment of the simulation model is of great importance, as will allow us to develop design techniques for our future MDPC.

Measures were done at the MIR region for a 3D modulated structure, and an interesting stop-band appeared at the 10 um region, indicating that the Ni structure worked as a useful PhC.

The software used to perform the simulation was the FDTD package MEEP [7] of the MIT. A simple model of the PhC structure was made employing a perfect metal, and agreement between real measures and simulations was acceptable. We found that in our working band the optical characteristics of the nickel suffered great variation, an effect not seen with perfect metal. Nevertheless, the results suggested interesting features that could be observed in the real measures.

IV. APPLICATIONS

We can enumerate both optical and electric applications for MDPH. The simplest applications are selective optical mirrors or filters, of interest in optical communications. The inclusion of electrodes can be used to create optical modulators and high quality factor, thus efficient, thermal radiators. Promising electrical application are capacitors, and thermally controlled devices.

V. CONCLUSION

In this work we present a successful MDPC working as a highly selective optical filter, along with the techniques used to fabricate it. We must point out that this process is still being optimized. The developed technique can be adapted to infiltrate other compounds into the mould PhC, what opens the possibility of new functionalities. Work is also done to include material loses in the simulations.

The use of metal in a PhC will improve PhC optical response, being a very promising path to further research.

REFERENCES


Figure 1. a) SEM micrograph of a Nickel filled MpSi PhC. b) shows the EDS analysis of the previous, where the red portion represents Si, and the green spheres are Ni.
Porous alumina covered by WO3 sputtered layer as sensing material for MEM gas sensor

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Abstract— In this work we report a micro hotplate gas sensor developed using a WO3 sputtered layer on nanoporous alumina as gas sensing material. This gas sensor has been characterized for hydrogen detection obtaining a good response at low working temperature.

1. Introduction
The gas sensing properties of metal oxide semiconductor materials have been the subject of research for many years [1]. The usual working temperature of such sensors is about 350ºC or higher so power consumption is generally an issue, especially if portable gas analysers are aimed at. Microsystems technology allows for developing micro-hotplate gas sensor substrates with lower power consumption because the area to be heated is very small and thermal conductivity within the membrane is very small. In this work we present a possibility to further improve micro-hotplate gas sensor performance by increasing surface area of the gas-sensitive film without increasing the area to be heated. This is accomplished by depositing a porous alumina layer (40 – 60 nm pore diameter) onto the membrane and conformably covering pore walls by a sputtered gas sensitive material (WO3).

2. Device developed
The fabrication procedure is as follows:
(1) Deposition of the membrane layer: A 0.3 μm thick Si3N4 layer is grown by LPCVD. Each chip has 4 membranes, with size of 900 × 900 μm2.
(2) Deposition and patterning of a POCl3-doped polysilicon heater.
(3) Deposition of a 0.8 μm thick SiO2 layer to insulate the heater from the active film.
(4) Patterning of the backside etch mask.
(5) Deposition of photoresist with open windows on the membrane areas.
(6) Successive sputtering of Ti (40 nm) and Al (380 nm).
(7) Anodization process (107 - 250 V) using tartaric and malonic acid as electrolytes. Growth of porous alumina. Pore widening step in HF.
(8) Lift off process for defining porous alumina onto the membrane areas only.
(9) Deposition of Pt interdigitated electrodes (figure 1,2)
(10) Deposition of the photoresist for the sensing material deposition.
(11) Deposition of WO3 layer by sputtering on top.
(12) Lift-off the WO3 film. (See figures 3 and 4)
(13) Backside silicon etching with KOH at 70ºC (40 wt%) to create the thermally insulated membranes.
(14) Wire bonding and packaging. Each chip is mounted on a TO-8 package.

Fig.1. Optical microscope image of the MEM gas sensor with the porous alumina on the membrane (5 x)
Fig.2. Optical microscope image of the porous alumina on the membrane (50 x)
Fig.3. Optical microscope image of the WO3 sputtered layer on the porous alumina layer (5 x)
3. Results and discussion

The response of the porous tungsten oxide microsensors towards 1000 ppm of hydrogen was studied at operating temperatures ranging from 50 to 350ºC. The response (defined as the resistance ratio $R_{\text{air}}/R_{\text{gas}}$) peaked at 1360 when the sensors were operated at 150ºC (see figure 5,6)

At present we are studying the response for low concentrations of H$_2$. In the future we will characterize the sensing layer morphology in the final device and we will study the humidity effect and the response to other gases.

4. Conclusions

This paper shows that the aluminum anodization is fully compatible with standard Microsystems technologies. Highly responsive hydrogen microsensors operating at low temperature (150ºC) have been obtained. This is possibly due to the specific chemical composition and crystal structure of the tungsten oxide films complemented by the dramatic increase in surface-to-volume ratio obtained via this technique.

The response time increases very quickly for low working temperatures but at about 225 ºC there is a good compromise between sensitivity and response – time.

References


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Fig.4. ESEM images of the porous alumina layer before and after WO$_3$ sputtering

Fig.5. Response to 1000 ppm H$_2$ at 250 ºC 200 ml/m

Fig.6. Sensor response to hydrogen 1000 ppm at different operating temperatures

Fig.7. Sensor response and response time to hydrogen 1000 ppm at different operating temperatures
Morphological and gas sensing characterization of nanostructured WO₃ gas sensors

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Abstract— In this article we show the process steps and the morphological and gas sensing characterization of gas microsensors, where the sensing layer is based on a nanostructured WO₃ layer obtained employing a nanoporous alumina sacrificial layer used as template. The sensing properties toward hydrogen at high and low concentrations, carbon monoxide, ethanol and humidity have been investigated. We have obtained very high sensitivity for hydrogen and low influence of RH.

INTRODUCTION

WO₃ films have been studied intensively in the last years for gas sensing applications, because this material shows high sensitivity for different interesting gases, like NO₂, other toxic gases or ethanol [1,2,3]. WO₃ can be deposited by RF sputtering and integrated in MEMS substrates [4]. Its application spectrum is quite wide, including portable gas sensing applications.

Power consumption of the traditional gas sensors is very high because operating temperatures are rather high (e.g. above 300°C). Micromachined gas sensors [5] allow for decreasing power consumption down to some miliwatts, but this is still too high for many applications. In this article we propose a technique to increase the area of the sensing material in contact to gases maintaining the low area to be heated. This technique is based in obtaining WO₃ nanodots grown on the active layer.

In this paper we discuss the morphological (ESEM and AFM) and gas sensing (H₂, CO, ethanol and RH) properties of the nanostructured gas sensors obtained.

EXPERIMENTAL

A. Sample preparation

The nanostructured gas sensors are based in a standard microhotplate generally employed as gas sensing platform. The fabrication procedure is as follows:

1. Deposition of the membrane layer: A 0.3 µm thick Si₃N₄ layer is grown by LPCVD. Each chip has 4 membranes, with size of 900 × 900 µm².
2. Deposition and patterning of a POCl₃-doped polysilicon heater.
3. Deposition of a 0.8 µm thick SiO₂ layer to insulate the heater from the active film.
4. Patterning of the backside etch mask.
5. Deposition of photoresist with open windows on the membrane areas.
6. Successive sputtering of Ti (20 nm), W (50 nm) and Al (500 nm).
7. First anodization process at 27 V, conducted at wafer level. Growth of porous alumina with self-organized nanopores.
8. Reanodization of the metals up to 90 V for growing tungsten oxide nanodots employing the nanoporous alumina overlayer as a template.
9. Removal of the porous alumina by selective wet etching.
10. Lift-off process eliminating the photoresist. As a result, the nanostructured tungsten oxide remains on the membrane areas only.
11. Annealing process in reactive atmosphere at 500°C. This process ensures that the whole surface of the nanostructured film is oxidized and crystallized.
12. Deposition of Pt interdigitated electrodes on top of the nanostructured film. Electrode gap is 50 µm.
13. Backside silicon etching with KOH at 70°C (40wt%) to create the thermally insulated membranes.
14. Wire bonding and packaging. Each chip is mounted on a TO-8 package.

B. Device characterization

Active layer morphology

Figure 1 shows a general image of the membrane of the micromachined gas sensor. It is possible identify the WO₃ active layer under the Pt interdigitated electrodes.

Figure 1. ESEM Image of the nanostructured sensor
Figure 2 shows an AFM image of the nanostructured active layer. The active layer shows a complex morphology. In big grains (500 nm diameter), generated by the deposition process of the pure tungsten (by RF sputtering) sit low diameter dots. A statistical analysis was conducted to estimate grain size (Figure 3). Using ImageJ software we concluded that 81% of small grains had a diameter ranging from 50 to 65 nm. The mean diameter of pores in the nanoporous alumina layer used as pattern was 60 nm. Therefore we can conclude that the low diameter grains are the nucleation of WO3 nanocolums (Figure 4).

Figure 2. AFM Image of the surface of the active layer

![AFM Image](image)

Figure 3. Grain diameter distribution

![Grain Diameter Distribution](image)

Gas sensing characterization

The work temperature - sensitivity dependence was studied for H2 at 1000 ppm in air (Table 1). The maximum sensitivity was obtained at 150 °C. This study was repeated for 20 ppm of H2 in air and again 1500°C was the optimal operating temperature. At such temperature, sensors were not responsive to 20 ppm of CO and response to ethanol 8000 ppm was half the one for H2 1000 ppm (Table 1). Furthermore, for low concentrations of H2 (from 0 to 20 ppm) at 150 °C, the response was very linear (r=0.999). Figure 5 shows the relative humidity (RH) sensitivity of the sensors. When moisture content is changed from 0 to 50% the sensor response is high, but when changes occur from 50 to 80%, humidity influence decreases dramatically. Therefore, these sensors can work in high RH environments.

<table>
<thead>
<tr>
<th>Op. temp. (°C)</th>
<th>25</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2, 1000 ppm</td>
<td>10</td>
<td>103</td>
<td>79</td>
<td>17</td>
<td>8.2</td>
</tr>
<tr>
<td>H2, 20 ppm</td>
<td>-</td>
<td>4.2</td>
<td>3.1</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>CO, 20 ppm</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethanol, 8000 ppm</td>
<td>-</td>
<td>51</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5. RH sensitivity of the final device

CONCLUSIONS

This paper shows a technique to make compatible the micromachined silicon technologies and porous alumina growth. This porous alumina is used as template pattern for obtaining a nanostructured active layer (WO3) for gas sensing applications. The active layer obtained is based in nanodots of WO3. Sensors are highly responsive to hydrogen at low operating temperature (150 °C).

ACKNOWLEDGMENT

Financial support from the Spanish Ministry of Science and Innovation via grant no. TEC2006-03671/MIC and the Catalan Government through grant no. 2005SGR-01084 is gratefully acknowledged.

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Electrically Controlled Metal Oxide Gas Nanosensor

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Thomas Haas
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Abstract—Conventional metal oxide gas sensors present problems in the distinction of oxidizing and reducing gases. More critical are their relative high operation temperatures which impede the integration into CMOS technology. By means of a nano-thin-film-transistor with a sensitive layer of $SnO_2$, we developed a gas sensor on the top of a CMOS chip with a substantial reduction on the operation temperature. With a sensitive layer thickness in the Debye length range, the electric field crosses the device reaches the surface and modulates the gas sensitivity.

I. INTRODUCTION

The capability of co-integrate a semiconductor gas sensor into CMOS circuitry is still a challenge due to the high operation temperature, necessary to adjust the sensor sensitivity. Because of this fact these devices are not able to be integrated into CMOS technology. However, some observations revealed that a high electric field led to sensitivity changes in such device. Our improve is to use these external electric fields and modulate the electrical gas sensitivity by means of changes on the energy levels (Fermi level) [1]. To enable this, the sensing layer thickness must be kept in the range of the Debye length (some tens nm), with these conditions, the electric field crosses the device and reaches the surface modulating the surface energy states. Because of this fact the sensor operation temperature is possible with relative low value (ranging from $150^\circ$C to $200^\circ$C) enabling its integration into CMOS technology.

II. DEVICE PROCESSING

Common to the sensor is a gated structure that provides an electrical control. It is insulated from the metal-oxide-semiconductor (resembles a MOSFET with an added sensitive semiconductor layer), see Fig.1. The technology implementation process consists in two steps [2]: Buried gate electrodes are fabricated using a standard CMOS processes. The platinum source-drain, temperature sensor, heater and the $SnO_2$ nano-thin-film are produced by standard thin-film deposition technology.

Materials characterization TEM and XRD examinations reveal a $SnO_2$ compact layer with grain size between 5 nm and 25 nm (Debye length is circa 6 nm, it means that sensor is close to the flat band limits). Sensitivity layer has a polycrystalline structure without preferred structure.

III. MEASUREMENTS

Using a nano-thin-film gas sensor based on field effect, the measurements were realized under synthetic air of 20% oxygen, 80% nitrogen with relativity humidity of 40% and temperature equal to $25^\circ$C. The sensor operation temperature was $200^\circ$C ($V_{Heater} = 12$ V) enabling measurements of oxidizing ($NO_2$) and reducing gases ($CO$). However dopants drift in the sensing layer under the exposition to high electric fields [3], therefore a unique measuring method was developed [4]. With this configuration, sensor was exposed to several gases with different concentrations, its response is drawn in Fig.2. It is obvious that the sensor presents better sensitivity to $NO_2$ with positive than with negative gate voltage as
the measurements shown, consequently the influence of the external electric fields in the gas adsorption is evident.

IV. DISCUSSION

In order to determine the number of strong chemisorbed particles, it is necessary to calculate the potential produces by them. As the concentration of the free charged carriers at the surface depends on the height of the intergranular barriers, changes in the resistance are correlated with changes on the band bending [5]:

\[ \Delta V_S = \frac{kT}{q} \ln\left(\frac{I_I}{I_F}\right) \]  \hspace{1cm} (1)

where \( I_I \) and \( I_F \) denote the drain current in absence and in presence of gas. One solution of the Poisson equation is:

\[ \Delta V_S = \frac{q \cdot (N^-)^2}{\varepsilon_o \cdot \varepsilon_r \cdot N_D} \]  \hspace{1cm} (2)

where the Schottky approximation was assumed. Finally the charged coverage is expressed as:

\[ \theta^- = \sqrt{\frac{\Delta V_S \cdot \varepsilon_o \cdot \varepsilon_r \cdot N_D}{q \cdot N_{Surf}^2}} \]  \hspace{1cm} (3)

Using Eq.3 the results are presented in Fig.3. In summary the adsorption of two gases \( NO_2 \) or \( CO \) in presence of \( O_2 \) is represented by continuous lines, on the otherwise point lines represent the response to three gases \( NO_2, CO \) and \( O_2 \) with different sequences of exposition. When a negative potential is applied the number of strong chemisorbed molecules of \( NO_2 \) is increased (related to the zero potential) on the other hand due to the application of a positive potential it is reduced. For \( CO \) occur the opposite, it is reduced with negative and increased with positive voltage. These external electric fields do not affect the reaction path of co-adsorption, only the reaction magnitude is modified under the exposition to high external electric fields. In presence of \( CO \) the strong adsorption of \( NO_2 \) is enhanced because \( CO \) reacts with \( O_2^{-} \) on the surface producing more free adsorption centres, the free sites can be occupied by \( NO_2 \). Moreover the presence of \( NO_2 \) produces a reduction in the number of \( O_2^{-} \) molecules reducing the reaction at the surface with \( CO \) [6].

V. CONCLUSION

External electric fields modulate the adsorption of gases on the semiconductor surface. They change the magnitude of adsorption increasing or reducing the reaction on the surface. However they do not present interference on the reaction path of co-adsorption as was proved here.

ACKNOWLEDGMENT

This work was supported by the german BMBF.

REFERENCES

OPTIMIZATION OF POLYMER COATINGS IN A SAW SENSOR ARRAY FOR CHEMICAL WARFARE AGENTS SIMULANTS DETECTION

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Abstract— Chemical warfare agents are a very dangerous weapon, but also, they are easily transported and hidden. This has increased the development of new technologies for their detection. Electronic noses based on Surface Acoustic Wave (SAW) sensors are cheap and fast systems for this purpose.

Keywords- SAW sensor; Electronic nose; LSER; Chemical warfare agent; Polymer

I. INTRODUCTION

Due to safety reasons, chemical warfare agents simulants were used (Table I). These are simulants of well known Chemical Warfare Agents such as Sarin (GB), Soman (GD) and Distilled and Nitrogen Mustard (HD, HN)[1]. Our goal was to design a SAW sensor array with high sensitivity and selectivity properties.

A. Theoretical background

SAW sensors are coated with different polymers, which behave in a different way depending on the volatile organic compounds (VOCs) they are exposed to. Sorption properties are characterized by the gas-polymer partition coefficient (K), which is the ratio between the vapor concentration in the gas phase and vapor concentration sorbed by the polymer. By the linear solvation energy relationships (LSERs) equation, this partition coefficient can be estimated [2]. Our sensor array optimization is based on the theoretical analysis of the partition coefficients of some of the most used polymers in gas sensing.

B. Statistical treatment

Principal Component Analysis (PCA) and a Probabilistic Neural Network (PNN) have been used for data analysis. Both were implemented in Matlab®. PCA is a linear method to reduce the dimensionality of the data. Once the analysis is done, all data can be plotted in two axes. The neural networks were trained and the performance was evaluated with leave-one-out cross validation.

II. EXPERIMENTAL

A. SAW Sensors

Each SAW sensor consist of an oscillator that is controlled by a Delay Line (DL) fabricated on ST-x quartz, which, in our case, has an oscillation frequency around 157 MHz. The Interdigitated

<p>| TABLE I: CHEMICAL WARFARE SIMULANTS |</p>
<table>
<thead>
<tr>
<th>Simulant</th>
<th>Abbreviation</th>
<th>Concentration (ppm)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl methylphosphonate</td>
<td>DMMP</td>
<td>0.05 – 1</td>
<td>C,H,O,P</td>
</tr>
<tr>
<td>Dipropylene glycol monomethyl ether</td>
<td>DPGME</td>
<td>0.5 - 10</td>
<td>C,O</td>
</tr>
<tr>
<td>Dimethylacetamide</td>
<td>DMA</td>
<td>30 – 200</td>
<td>C,H,NO</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>DCM</td>
<td>50 – 200</td>
<td>C,Cl</td>
</tr>
<tr>
<td>1,5-Dichloropentane</td>
<td>DCP</td>
<td>5 – 100</td>
<td>C,C,H,Cl</td>
</tr>
<tr>
<td>Toluene</td>
<td>TOL</td>
<td>50 – 200</td>
<td>C,H,</td>
</tr>
<tr>
<td>1,2-dichlooroethane</td>
<td>DCE</td>
<td>80 - 200</td>
<td>C,H,Cl</td>
</tr>
</tbody>
</table>

<p>| TABLE II: SAW SENSOR ARRAY COMPOSITION |</p>
<table>
<thead>
<tr>
<th>Sensor number</th>
<th>Polymer</th>
<th>Thickness(Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Reference</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>PCPMS</td>
<td>150</td>
</tr>
<tr>
<td>2</td>
<td>PECH</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>Carbowax</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>PDMS</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>PEI</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
<td>PMFTPMS</td>
<td>250</td>
</tr>
</tbody>
</table>
Transducers (IDTs) were made of aluminium deposited by RF sputtering using photolithographic techniques, being the thickness 200 nm. Both the spacing between the fingers and their width were 5 µm, what means a 20 µm wavelength, \( \lambda \).[3]

**B. Polymer coatings**

SAW sensors were coated those polymers resulting from the optimization method (Table II). They were deposited on the sensors by spray coating. The thickness of the films was set to 100 nm (300 KHZ), although a lower thickness was deposited on those that showed high losses. All polymers were commercially available. These polymers have already shown good permeability and solubility properties.

**C. Data acquisition and instrumentation**

Our setup is composed of a gas line, two flow meters, one frequency counter, thermal bath and the sensors chamber. Samples arrived to the chamber in air dilution. Vapor concentration in air is controlled by a 10 ml/min flowmeter. Data are acquired in a computer by a home-made software, which also measures the temperature in both, the sensor chamber and the environment. Samples were kept at constant temperature for 30 minutes (headspace time) before being carried to the chamber. Air flow was constant in the chamber (200 ml/min) at any time. Exposure time was 15 minutes, and the temperature in the sensor chamber was kept at 23º C by a Peltier device. Every simulant was measured repeatedly for different concentrations (Table I).

**III. DISCUSSION AND RESULTS**

Consequently to the partition coefficient definition, a linear relation between frequency shift and vapor concentration is expected. Fig. 1 shows an example of this behavior. Every couple polymer-VOC has a different slope. Therefore a specific print for each simulant can be composed (Fig 2). We applied Principal Component Analysis (PCA) to our data. A good separation is observed (Fig 3). According to our theoretical analysis for the array optimization, good selectivity and sensitivity skills have been achieved. As seen in Fig 4, simulants have been clearly discriminated by PNN.

**ACKNOWLEDGMENT**

This work is being supported by the Spanish Education and Science Ministry under the project TEC2007-67962-C04-02

**REFERENCES**


Abstract—We use finite elements simulations in order to study the fluid flow behaviour in a chamber of a preconcentrator. We realised that most part of the fluid does not affect our preconcentrator because it is going out the chamber at high distance above it and parallel to the preconcentrator. So, we are wasting most part of our fluid and we need a lot of time to have a good concentrator factor. We propose a chamber modification that forces the fluid to go near the preconcentrator and perpendicular to it, thus, improving concentration factor almost twice. With this new design we are able to concentrate more analyte in the same period of time.

Keywords— Preconcentrator, fluid flow simulation, concentration simulation.

I. INTRODUCTION

Several toxic gases such as benzene are dangerous at low concentrations. At present, gas sensors are not able to detect concentrations on the limits required. That is why the design and implementation of preconcentrators is an important task. [1-4]

A preconcentrator is used to adsorb these traces of toxic gases during a period of time. Then, the full amount of adsorbed gas is released by means of a temperature step in the absorbent material, thus obtaining an increased concentration detectable by gas sensors. We decided to simulate the chamber that we were using in experimental measurements in order to see the fluid flow behaviour. Thanks to simulation we realised that the gas sample to be sensed flew parallel to the preconcentrator surface, so most part of the analyte to be detected did not affect the absorbing material. We propose a new chamber design, by means of simulations, which was more efficient and economic that developed different chambers. Our proposal improves the chamber design forcing a larger amount of the sample flow to interact with the absorbent material increasing the concentration factor almost twice more.

II. EXPERIMENTAL CHAMBER

We have a cylindrical 6-mm diameter 3.8-mm height chamber. It has input and output 1.27-mm diameter tubes situated at 2 mm above the base (See Figure 1a). Preconcentrator is located at the base. This is a 4 mm side square of porous alumina substrate with activated carbon deposited on top (See Figure 1b).

In the experimental set up, we introduce the preconcentrator in this chamber; a 100 ml/min flow of 150 ppb of benzene diluted in CO₂ is injected during 10 minutes at ambient temperature, so the preconcentrator is adsorbing the analyte. Then we force a 100 ml/min flow of helium and we heat the preconcentrator to desorb all the benzene adsorbed in the material. Nowadays, we are using a gas chromatograph mass spectrometer (GCMS) to measure the desorption peak.

III. FLUID FLOW SIMULATION

In order to study fluid flow behavior inside the chamber, we are coupling different models of Comsol Multiphysics; Weakly Compressible Navier-Stokes model for fluidic and Convection and Diffusion model for concentration.
We use the Weakly Compressible Navier-Stokes model for fluid flow because velocity of fluid depends on density variations (Equation 1). We introduce laminar velocity as input and constant pressure as output boundary condition. With the Convection and Diffusion model we simulate the concentration variations. In the preconcentrator there is a two-way reaction which converts free analyte ($A_f$) to analyte on the wall ($A_w$). This is governed by the velocity of reaction which also depends of temperature (Equation 2).

$$\nabla \cdot (\rho u) = 0 \quad (1)$$

$$A_w \xrightarrow{k_- off} A_f \xrightarrow{k_+ on} W \quad (2)$$

Next function must be fulfilled in our preconcentrator as boundary condition in order to model the adsorption and desorption processes using a linear function:

$$\frac{\partial C_{aw}}{\partial t} = -k_- off \cdot C_{aw} + k_+ on \left( C_{max} - C_{aw} \right) \quad (3)$$

In Figure 2a we can see the streamline of velocity field. Most part of the air crosses the chamber without affecting the preconcentrator because the main flow is at a relatively large distance of the preconcentrator.

### IV. CHAMBER MODIFICATION

In order to improve this, we will use a “wall” which forces the air to go down near the preconcentrator surface (See Figure 2b).

In Figure 3 we compare the amount of benzene adsorbed without wall and with the wall placed in the middle of the chamber.

In Table 1 we can see the value of counts during the adsorption phase. This is the amount of analyte going out of the chamber. $\Delta$ Counts is the difference between input and output analyte, so, with this value we extract the percentage adsorbed and the improvement is related to this.

<table>
<thead>
<tr>
<th></th>
<th>Analyte out (u.a.)</th>
<th>Analyte input- output (u.a.)</th>
<th>Amount of analyte adsorbed (%)</th>
<th>Retention factor improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without wall</td>
<td>0.1088</td>
<td>0.0185</td>
<td>14.53 %</td>
<td>1</td>
</tr>
<tr>
<td>With wall</td>
<td>0.0944</td>
<td>0.0329</td>
<td>25.84 %</td>
<td>1.78</td>
</tr>
</tbody>
</table>

This wall improves the preconcentrator adsorption capability in a 1.78 factor. So, using this wall, we are able to adsorb more analyte in the same period of time. Experimentally, we have obtained an improvement of 1.85 factor, which is near to the simulation results.

### V. CONCLUSIONS

We have detected a problem which was unknown by means of simulation. By using a new design we are able to absorb more analyte in the same period of time than with our previous design. Experimental measurements realised with the GCMS have validated our simulations, This simulations more economic, faster and simpler than experiments have contributed to understand the problem and to propose solutions.

**ACKNOWLEDGMENT**

This work is financially supported by the Science and Education Spanish Ministry (TEC2006-03671)

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Micro-nanotechnologies: An approach to develop In Vitro Diagnostic Devices

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Abstract—A symbiosis of microfluidics, biosensors, and ICT technologies presents interesting solutions for the development of "Disposable quick and reliable diagnosis cards" applicable to the field of health and food. The research activity has already yielded results that cover the entire process of diagnosis, from the sample preparation, concentration and amplification of DNA (microPCR) to the detection.

Keywords-component; Fluid handling, Sample preparation, Smart systems.

I. INTRODUCTION
There is a clear need to provide portable diagnostic tools to ensure rapid, affordable and simple analysis in many scenarios of our society (hospitals, airports, doctor’s practice, roadside police controls, and natural environment). Currently, portable devices are based on low sensitive immunochromatographic strips or low sensitive electrochemical detection systems, whereas desktop systems are sensitive and automatic but bulky, heavy and expensive. Hence, owing to the new advances in polymer microfabrication and its synergy with Information Communication Technologies (ICT), this talk will show how is possible to prioritise and combine integrated sample preparation, low cost manufacture and ICT devices. This combination creates an intelligent and portable system across many sectors for efficient health treatment, high productivity food processing and secure environment monitoring.

II. DESIGN AND DEVELOPMENT
Regarding fabrication, typical microfluidic chips depend on expensive substrates that come from the microelectronic industry. As a consequence, it is necessary to use expensive equipment with relative low throughput due to large microfluidic footprint needed. This high cost makes unaffordable to break into the market with a large enough disposable LOC that includes automated sample preparation subcomponents (microchannels, integrated valves, reagents, and pumps). This lack of sample preparation limits their potential and market impact. The fabrication technology used by our group stacks several layers of different polymers without any expensive substrate. This process produces a 3D polymer microfluidic circuitry.

In general, the concept of a IVD-POC device requires a set of technologies to cover, in an efficient way, the different topics, being the most relevant: disposable chip, biomarkers, biosensor and the reader/controller.

In our group, the chosen approach implies to work on the 5 Base Technologies shown in the picture:

From the functional point of view, sample preparation integrated in the labcard, is a critical issue. The integrated sample preparation results so far are: (i) a PCR LOC where sample preparation (concentration and lysis) and PCR has been developed in one chamber using faecal sample; (ii) RT-PCR LOC where a RNA has been extracted and amplified using saliva swabs; (iii) a set of microfluidic control components integrated in previous devices; and (iv) hollow needles with electrodes on them to monitorise the cell death.

In terms of ICT convergence, the user will obtain the results of the tests by connecting the Labcard reader to a very popular interface (a smartphone), creating a new instrument namely “The SmartBioPhone™”. All standard smartphone capabilities are at the disposal of the point of care instrument.

ACKNOWLEDGMENT (HEADING 5)
This activity is carried out under the Basque programs ETORTEK and EMAITEK and also the European FP6-7 programs (OPTOLABCARD, LABONFOIL, SMARTHEALTH and PORFASTFLU)
Abstract—In this document, the development of fluidics microsystems in the Department of Electronic Engineering at the University of Seville is reported. The research lines of this group focus on silicon devices for massive microparticle generation using the flow focusing technique. In addition, this group is interested in systems for fluid impulsion and extraction. In this field, a device fabricated of PDMS, poly(dimethilsiloxane), has been developed. Lastly, microfluidic devices with similar behavior as microelectronic ones is another issue of interest.

Keywords—microfluidics; microparticles; extraction; impulsion.

I. INTRODUCTION

The Microsystems Group of the Escuela Superior de Ingenieros Department of Electronic Engineering has several lines of research, one of which involves the development of fluidic microdevices. In this line, the design and fabrication of silicon devices for multiple generation of microparticles are carried out in collaboration with the Centro Nacional de Microelectronica (IMB-CNM) of Barcelona, Spain. The fabrication using silicon as base material has been performed by CNM, while the Microsystems Group of Seville employs its fabrication facilities on polymer materials, e.g., PDMS poly(dimethilsiloxane) and SU-8 photoresist. In this polymer fields, a system for fluid extraction and impulsion using Venturi effect has been designed and fabricated using PDMS.

This document presents a summary of the commented devices. In microparticle generation, flow focusing method is reported. In addition, the development of multiple flow focusing devices on silicon and its stabilization are commented. Finally, a Venturi device for extraction in the submicroliter range is reported.

II. MICROPARTICLES GENERATION USING FLOW FOCUSING

The flow focusing technology [1] consists on the use of two immiscible fluids so that the reduction of stream of one of these fluids, core fluid, by another fluid, shell fluid, is achieved. Then, due to surface tension, the stream of core fluid breaks into droplets, Fig. 1. If chosen fluids are air as shell fluid, and water as core fluid, the aim would be to generate water droplets into air.

The diameter of the droplet can be calculated by the following equation:

$$d_g = 1.89 \cdot \left( \sqrt{Q_c} \right) \cdot \sqrt{\frac{8 \cdot \rho_c}{\pi^2 \cdot \Delta P}}$$

Where $Q_c$ is the flow rate of core fluid, and $\rho_c$ is its density. And $\Delta P$ is the pressure drop for shell fluid.

The interest of this technique is the multiple generation [2,3,4] because this way, massive production can be achieved at a lower cost. In parallel flow focusing devices, the arising of instability between different outputs has been observed. Due to this phenomenon, the diameters of the droplets from different orifices are different, and the product loses one of its main advantages, namely the monodispersion in droplet diameters. This group has contributed to the solution of this problem by adding pressure drops (fluidic resistors) in the inlet of the devices [4,5]. In Fig.2 a multiple flow focusing device without top cap is shown.
Extraction and impulsion polymer microdevices for lab on chip applications are investigated. In this line, a PDMS device for controllable extraction in the submicroliter range has been developed [6] and it can be seen in Fig.3. This PDMS structure requires an aspiration tube, and a top cap because otherwise the thin membrane would deflect due to pressure and Venturi effect would not happen. In addition, the holder prevents the membrane from breaking. This holder is made using methacrylate with orifices for the tubing connection.

The extraction of a working fluid is accomplished by putting the fluid reservoir in contact with a membrane, which is controllably deflected, extracting the fluid out of the reservoir. The deformation of the membrane is produced by the generation of a negative pressure in the side opposite to the working fluid. This negative pressure is generated from a positive pressure source by using the Venturi effect. A cross section of the device with the top cap and the aspiration tube, and the working principle are depicted in Fig.4.

Finally, the curves which define its behavior are shown in Fig.5.

The maximum extracted volume is 120 nL for a membrane with a diameter of 2500 µm. The maximum volume fits with a driving pressure of 800 mbar and the average extraction ratio for the device with a membrane with a diameter of 2500 µm is 220 pL/mbar.

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GMR Current Sensors for IC applications

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Abstract—Giant MagnetoResistance (GMR) based emerging technologies have appeared as potential substitutes for Hall based devices as magnetic field sensors. We are now reporting on recent results regarding the applicability of GMR based electrical current sensors at the integrated circuit (IC) level. In this sense, different prototypes are analyzed, including electrical and magnetic characterization, modeling and testing in real applications such as analog isolators or IC wattmeters.

I. INTRODUCTION

Nowadays, novel technologies are demanding current sensors with high level of integration and compatibility with the classical CMOS technology. As examples, we can consider the inclusion of these mili-Ampmeters in GMR based systems-on-chip (SoC) for biological applications or the need of built-in current sensors (BICS) for built-in self testing of different families of integrated circuits (IC) [1]. In the present work, we demonstrate the potentiality of GMR based full Wheatstone bridges for low current monitoring at the IC level. With this goal in mind, a number of prototypes has been specifically designed, fabricated and tested.

II. DEVICES DESCRIPTION

A. GMR structures

Different GMR mechanisms and their associated layered structures have continuously emerged during these years. Among them, two have demonstrated to be useful in a major range of applications: spin-valves and (SV) and magnetic tunnel junctions (MTJ) [2]. Their compatibility with standard CMOS technology is in the basis of this rapid growth. Both structures share the GMR principle: a 'giant' dependence of its electrical resistance with the external magnetic field. A SV consists of two ferromagnetic layers, separated by a nonmagnetic conductor spacer, usually Cu. This case, current flows parallel to the planes. A MTJ consists of two ferromagnetic layers, separated by an oxide isolation layer. This case, the current flows perpendicular to the planes and crosses the isolating barrier by tunnel effect. In both cases, an external magnetic field changes the relative orientation of the magnetization vectors and, consequently, the resistivity.

B. Sensors layout

Being GMR sensors resistive, a Wheatstone configuration is preferred [3]. The current-to-be-measured is driven through the magnetoresistive sensing elements by means of specifically designed metallic strips, implemented into the chips during the fabrication process. The microelectronic fabrication process of the devices consisted of five lithographic steps. In the first one, the GMR elements are patterned by direct laser writing on photoresist followed by ion milling. The aluminum contact leads are then sputter deposited and then defined by lift off. A SiO$_2$ layer is then deposited, for isolation. In a second metallization level, the current carrying meander tracks are sputtered and defined by lift off. A second sputtered Al$_2$O$_3$ layer is used as passivation. Contact pads are defined and opened by wet etching. Micrographs of representative devices are displayed in Fig. 1.

III. CHARACTERIZATION

So fabricated devices are cut into dices and then soldered and encapsulated into chip carriers. The workbench consisted of a GPIB controlled setup with a personal computer, a power supply (PS2521G, Tektronix), a standard magnetometer, a current source (220, Keithley), a data acquisition switch unit (34970A, Agilent) and some multimeters (34401A, Agilent). Principal parameters are collected in Tab. I. For high currents, self-heating effects appear. A thermal characterization was performed with the help of a climatic chamber (ACS, CH600) from -20 to +60°C, and the results are also shown in Tab. I.

IV. SENSORS MODEL

Electrical models of these devices are being developed in parallel [4]. Because of the particular characteristics of GMR based devices, Verilog-A, a high level language with analog
TABLE I
SV BRIDGES CHARACTERIZATION PARAMETERS (FROM [6])

<table>
<thead>
<tr>
<th></th>
<th>SN</th>
<th>SW</th>
<th>PN</th>
<th>PW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insertion resistance (Ω)</td>
<td>31.4</td>
<td>12.1</td>
<td>15.5</td>
<td>8.7</td>
</tr>
<tr>
<td>Sensor resistance (kΩ)</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>R sensitivity (%/mA)</td>
<td>0.126</td>
<td>0.013</td>
<td>0.046</td>
<td>0.006</td>
</tr>
<tr>
<td>Offset voltage (mV/V)</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>Linearity (±10 mA)</td>
<td>0.9999</td>
<td>0.9999</td>
<td>0.9991</td>
<td>0.9998</td>
</tr>
<tr>
<td>Sensitivity (mV/(V·mA))</td>
<td>1.150</td>
<td>0.103</td>
<td>0.522</td>
<td>0.050</td>
</tr>
<tr>
<td>Linear range (mA)</td>
<td>±15</td>
<td>±100</td>
<td>±25</td>
<td>±150</td>
</tr>
<tr>
<td>TCR (%/°C)</td>
<td>-0.11</td>
<td>±0.12</td>
<td>±0.12</td>
<td>±0.11</td>
</tr>
<tr>
<td>TCVoff (μV/°C)</td>
<td>-7.0</td>
<td>±5.1</td>
<td>±3.1</td>
<td>±3.5</td>
</tr>
<tr>
<td>TCS (%/°C)</td>
<td>-0.15</td>
<td>-0.14</td>
<td>-0.13</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

Fig. 2. Verilog-A model for a SV Wheatstone bridge

reinforcement is selected. A preliminary developed model for a bridge is depicted in Fig. 2.

V. APPLICATIONS

A. Current sensing

The more straightforward application of these devices is as current meter. A summary of results for SV devices is displayed in Fig. 3.

B. Analog isolators

We have also studied the possibility of using MTJ based full bridges in order to design analog magnetically coupled isolators. Representative results are shown in Fig. 4.

C. Power measurement

Moreover, we propose the use of GMR based sensors as basic multipliers in order to develop instantaneous power meters for IC applications. By using previously described SV based sensors, and with the arrangement depicted in Fig. 5, powers in the range 1 mW–500 mW can be measured.

VI. CONCLUSION

GMR (SV and MTJ) based current sensors have demonstrated their potentiality at the IC level.

ACKNOWLEDGMENT

Part of the work has been carried out under projects: HP2003/0123 (Ministry of Science and Technology, Spain), GV05/150 (Valencian Regional Government), TIC-3580 ((Junta de Andalucía Excellence Research Project)) and ENE2008-06588-C04-04 (Ministry of Science and Innovation, Spain and European Regional Development Fund).

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It is now fully assumed that Silicon Carbide (SiC) is one of the main semiconductors for next generation of power devices and systems. Most of the Power Semiconductor Manufacturers are now developing such devices and several commercial applications already include these components. However, SiC material also offers attractive properties for other applications, such as high temperature sensors and biomedical devices. Its chemical inertness, its good mechanical properties, its transparency to visible light, its non toxicity and biocompatibility makes SiC highly suitable for the biomedical domain. Several devices have been already demonstrated [1, 2]. In this sense, the first device we developed is the Platinum electrodes impedance sensor for in-vivo monitoring [2] or for cell culture. We used semi-insulating 3” hexagonal SiC wafers as starting material. Regarding cell culture sensors, in addition to the biocompatibility of the SiC, we also take profit of the transparency. In order to improve the device performances, the next development step was to grow Carbon Nanotubes (CNT) on top of the Platinum (Pt) electrodes used for sensing.

In parallel to these developments, SiC has been also investigated as a potential MEMS material. Its high Young modulus enables reaching higher frequencies and quality factors than those from Si devices, thus being beneficial for applications requiring high sensitivity [3], such as mass sensors. Recently, we have also developed an all electric actuation/detection SiC cantilever based on a capacitive scheme. The next step will be to study the different possibilities of a circuitry integration to get SiC devices similar to those on Si material recently fabricated at CNM [4]. This should open the route to portable SiC sensors able to operate in harsh environment.

References
Optical Fiber Humidity Sensor based on
Electromagnetic Resonances

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Abstract- A new optical fiber humidity sensor based on electromagnetic resonances in the infra-red region is presented here. This device has been made with an indium tin oxide coating that supports the electromagnetic resonances and a polymeric film that shows high sensitivity to relative humidity changes. The device shows a very good dynamical range and linearity.

Keywords- humidity sensor; optical fiber; electromagnetic resonance; ITO; layer-by-layer

I. INTRODUCTION

Humidity sensors have a great interest due to the several applications that need them to operate, such as air conditioning systems, medical diagnosis, agriculture, food quality preservation, etc. This fact has motivated a great advance in this field in the last years [1].

The utilization of optical fiber to fabricate sensors have revealed as a very good alternative to traditional electronic sensors because of its specific features, as simplified design, electromagnetic immunity, multiplexing, miniaturization, remote sensing, etc. These advantages have been exploited by many authors [2]. Although there are a wide range of optical fiber structures that are used to fabricate sensors [3-5], wavelength based techniques overcomes the limitations of amplitude based techniques, e.g. high sensitivity to power fluctuations or external noises.

In this work, an optical fiber humidity sensor (OFHS) based on electromagnetic resonances (EMR) has been developed. To fabricate the EMR supporting device, an indium tin oxide (ITO) coating has been deposited onto the multimode fiber core. An EMR absorption peak, which shifts to different wavelengths when the external refractive index varies, appears in the near infra-red region.

A polymeric film is deposited onto the ITO coating to complete the sensor structure. The refractive index of this layer is sensitive to relative humidity (RH) variations in the surrounding medium, so the EMR absorption peak of the final device shifts when the external RH changes. This sensor shows a dynamic range of 64 nm when the RH changes in the range between 20 to 80% and a high linearity.

To our knowledge, this is the first time that an OFHS based on EMR has been fabricated using an ITO coating.

II. EXPERIMENTAL

A. Device Fabrication

The fabrication of the sensor consists of three different steps. Firstly, a multimode optical fiber (Thorlabs Inc.) fragment is ultrasonically cleaned and its cladding is chemically removed. After that, an ITO coating is deposited onto the 200 µm optical fiber core by using a sol-gel method previously developed by Ota et al. [6]. This EMR supporting layer is made of 10 layers of ITO and has a thickness of 115 nm. To finish the structure, a PAH (poly-allylamine hydrochloride) and PAA (poly acrylic acid) sensitive structure is deposited by means of the Layer-by-Layer (LbL) technique [7]. This multilayer film has a refractive index sensitive to the relative humidity of the surrounding medium. In Fig. 1, a scanning electron microscopy (SEM) image of the sensor structure is shown. The three different parts of the device (fiber core, ITO coating and polymeric layer) can be distinguished.

Finally, the sensing structure is spliced in its both extremes to 200 µm-core pigtails to obtain the final device, which is shown in the schematic representation in Fig. 2.

B. Sensor Characterization

The experimental setup used to characterize the device is shown in Fig. 2. It is the typical optical fiber transmission setup with a white light source (DH-2000, Avantes Inc.) as optical power source and a near infra-red spectrometer (NIR 512, Oceanoptics Inc.) connected to a PC for collecting the data.

Figure 1. SEM image of a transversal section of the sensor
Figure 2. Experimental setup used to measure the sensor response

The sensitive device is introduced into an environmental chamber (Angelantoni Inc.) in order to subject it to humidity variations in the range from 20 to 80% RH.

III. RESULTS

The polymeric layer made of PAH and PAA, has the ability to change its refractive index when the external RH varies. This effect is due to the swelling-deswelling phenomenon that occurs at the polyelectrolyte film when absorbs or desorbs water from the surrounding air. The EMR absorption peak shifts to higher wavelengths when the RH rises because of this effect, as can be observed in Fig. 3. This peak is centered at 1184 nm when the external RH is 20% and at 1248 nm when the RH rises to 80%. This means a dynamical range of 64 nm in this RH interval, what is equivalent to a sensitivity of 1.066 nm/%HR.

In Fig. 4, the maxima of the absorption peaks when the RH is varied from 20 to 80% are represented (RH rise: blue line. RH fall: pink line). It can be observed in this graph that the hysteresis is low and both lines are very close. It is important to remark the high linearity of the device when the RH reaches values greater than 40%.

IV. CONCLUSIONS

In this work, a new OFHS is presented. The device operation is based on EMR in the infra-red region. An ITO coating makes possible the apparition of an EMR absorption peak sensitive to changes in the refractive index of the surrounding medium.

ACKNOWLEDGMENTS

The authors acknowledge financial support to the Spanish Ministry of Education and Science-FEDER TEC2006-12170 and TEC2007-67987-C02-02/MIC and FIDENA for the utilization of the SEM.

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Flow injection analysis devices for total phenolic compounds measurement

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Abstract—The basic design of the proposed biosensor was based on the measurement of the consumed oxygen in the reaction catalysed by enzyme Benzenediol:oxygen oxidoreductase (polyphenol oxidase, laccase). Such enzyme was immobilized on a minicartridge and the consumption of oxygen in the carrier buffer was registered by an oxygen meter probe. Two modes of operation have been developed. Flow injection analysis (FIA) was found to be very quick; however sequential flow injection analysis (SFIA) achieved better sensitivities. The best operating conditions have been established and the effect of ethanol and other molecules present in wine has been evaluated. The main phenols analysed showed a very similar response.

Keywords- Phenolic compounds; flow injection analysis; Laccase

I. INTRODUCTION

Phenolic compounds are widespread in plants. There are a wide variety of them in grapes and wines. Quantity and type of each of them depends on several factors such as variety of grape and procedure followed for wine-making [1, 2]. They play a very important role in the development of flavour, colour and stability of must and wine. Each wine can be characterised by the complexity of their phenolic composition. One of the routine quality controls usually carried out in wineries is the phenol analysis. Permanganate index is usually used although this titulation is not very accurate. The colorimetric procedure based on the folin-ciocalteau reagent is more specific for phenolic compound analysis. Design of biocatalysts by integrating enzymes allows the increasing of specificity for phenolic compounds and reduces the time consumed per analysis [3].

The objective of the present study was the design and implementation of bio-systems for the rapid quantification of total phenolic compounds in wine.

II. MATERIALS AND METHODS

The design of the biosensor was based on the measurement of the consumed oxygen in the reaction catalysed by the enzyme Benzenediol:oxygen oxidoreductase (polyphenol oxidase, laccase), using as substrates phenolic compounds. Commercial laccase, Suberase, kindly offered by Novozymes, was immobilised in Eupergit C by random covalent binding between epoxy groups from the matrix and hydroxyl, sulphhydryl and amine groups from the enzyme. Once immobilisation process was finished the enzymatic matrix was transferred into a chromatographic minicartridge (mobicol, MoBiTec GmbH). Minicartridge was placed “on line” in a flow injection analysis system, comprising a peristaltic Masterflex C/L pump flowing a carrier buffer (continuously saturated with air by a pump) to a Bio-Rad injection valve, used to inject the samples (100 mL) into the system. Once samples reached the enzymatic cartridge phenols were oxidised by laccase (the consumption of oxygen is proportional to the quantity of phenols oxidised). The consumption of oxygen was measured by using an oxygen meter probe. This probe was settled in a flow cell and connected to the correspondent oxygen controller (Strathkelvin Instruments) The system allowed working in two different modes. First option was flow injection analysis method (FIA), second option was sequential flow injection analysis (SFIA) In the latter case, once the sample was injected into the system and reached the enzyme minicartridge, system stopped, and the sample kept in the enzyme reactor during five minutes. After that time, system was re-started and the reaction measured.

Reaction time was analysed in both the FIA and the SFIA systems. Proper carrier flow-rate was analysed too. The effect of ethanol and the interferences caused by other molecules which may appear in wine were studied, as well as the effect of several phenols in the measured response.

III. RESULTS AND DISCUSSION

Effect of flow-rate was analysed previously to establish the working parameters, as well as the effect of ethanol in the response of the system. It was observed that response was greater as flow-rate decreased. Decreasing in flow-rate led the system to keep in contact phenolic substrates and Suberase for a longer time, resulting in higher oxygen consumption. A flow-rate of 1.4 mL/min was chosen as appropriate as responses were obtained in a shorter time. In the same way it was observed that ethanol concentration affected the response of the biosystem. At 10% (v:v) ethanol the response was significantly lower than at 1%. In fact, ethanol was necessary to get the maximum activity. Samples without ethanol resulted in a lower response too.
Biosystems were calibrated using gallic acid as model phenolic compound. The FIA system allowed a very fast response, taking no more than 2 min per sample. Samples were diluted (1:9, v:v). Direct results fitted a straight line from 50 to 500 ppm, covering typical phenolic concentrations found in wines.

The SFIA system allowed fast responses too. Seven minutes per sample were enough to accomplish the analysis, being capable of detecting very low concentrations of phenolic compounds. Data were fitted to a straight line from 1 ppm to 500 ppm.

The effects of several compounds usually found in wine were analysed. Only ethanol and glycerol (Fig. 1) showed a significant effect on response, increasing it when samples were 10-fold diluted. Several phenolic compounds were compared too. No significant differences were observed between gallic, coumaric, vanillic acids and trans-resveratrol; ferulic and syringic acids got the same response too.

![Figure 1](image)

Figure 1. Response of different compounds usually found in wine (A). Phenolic compounds measured using the FIA system. All of them were injected at 100 ppm (B).

IV. CONCLUSIONS

This method could be used for the analysis of total phenols in wines and fruit juices. Compounds usually present in such beverages do not affect significantly the response of the device.

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Thermal Behavior of a Heat-actuated Microcantilever

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Abstract—Thermal actuators have found a wide range of applications due to its advantages, including: large output force, displacement, easy implementation and CMOS compatible fabrication. This work considers T-shape silicon microcantilever resonators that are driven by thermal actuators. Our approach, temperature gradient actuation, exploits internal mechanical moments induced by temperature gradients due to Joule heating induced by driving an electric current through a heating element. This paper reports design, fabrication and electrothermal characterization of a heated T-shape silicon microcantilever in air.

Keywords: microcantilever, resonator, thermoresistors, actuation

I. INTRODUCTION

Thermally actuated compliant mechanisms are those onto which thermal loading is applied in order to deform a structure. A typical way of obtain a thermal load is to apply a current through a resistive material, heating this up (Joule effect). This type of thermally actuated compliant mechanism is known as electrothermal-compliant (ETC) [1, 2]. Several types of electrothermal-compliant actuation have been studied and demonstrated: bi-material or bimorph, hot/cold arm, thermal buckling and temperature gradient actuator (See Figure 1). Bi-material or bimorph actuators exploit the difference in thermal expansion coefficients of two materials bonded together. When a current is applied, the temperature of the bimorph is raised; one material will expands more than the other resulting in thermal stresses at the interface leading to bending of the structure. In the Hot/cold arm actuator when a current is passed through, the hot arm (higher resistance), heats up more than the cold arm (lower resistance). The difference in the thermal expansion between the two arms induces a deflection of the entire structure. The thermal buckling actuator consists of pairs of straight beams (legs) that are each connected to an opposite side of a shuttle, and are clamped at their far edge, when the legs are heated by passing an electric current through them, the resulting joule-heating induced thermal expansion moving the shuttle. The temperature gradient actuator exploits internal mechanical moments induced by temperature gradients due to Joule heating produced by a heater placed on the anchorage [3, 4]. This fourth approach is the one used in this work.

In order to obtain a dynamic response the actuators can be heated and cooled by periodic electric signals. In contrast to the three first types of ETC actuators, the heating is produced over a confined region, in the temperature gradient actuation scheme (primarily under and near the heater). Therefore this type of actuation has a shorter response time that the required to heat or cool the entire structure [4, 5, 6].

Figure 1. Types of electrothermal-compliant actuators.

II. DESIGN AND MODELING

The T-shape cantilever resonators were designed as a structure formed by 3 cantilevers of 350μm long, 32μm wide and 15μm thick that are hold together by means of an extra, rectangular mass of 50μm long, 300μm wide and 15μm thick. The resonator is actuated by two heaters placed on each external beam (see Figure 2). The footprint of the heater fits into a square with dimensions 40μm×16μm. It is a U-shape resistor made of heavily Boron-doped silicon cover with oxide. When an electric current is applied through the resistors it heats up, inducing a temperature gradient causing a mechanical moment and moving the free end of the cantilever.
III. EXPERIMENT AND RESULTS

Thermal and electrical characterization was performed. First, in order to calibrate the resonator, resistors values with respect to the ambient temperature were measured. The cantilevers were placed inside an oven (KEITHLEY74) and the resistance value was measured (FLUKE 89IV multimeter) as the temperature was progressively increased (see Figure 3). The linear relationship indicates an average variation of 0.0013 kΩ per ºK.

For the electrical testing, the heaters were excited with DC voltage in order to test the cantilever steady state response. An Infrared (IR) camera (AGEMA Thermovision THV-900 SW TE) was used to measure the temperature on the structure. The devices were painted with black matt paint with known emissivity of 0.98 in order to obtain a real temperature map. Figure 4 shows infrared IR microscope images of the heatable cantilever. The IR image was made with the cantilever heated, in air at ambient pressure.

IV. CONCLUSIONS

In this paper we designed and modeled a relatively straightforward to fabricate heat-actuated microcantilever IC processing technology compatible. The thermal and electrical experimental results show that this device can reach 500ºK (~350mW each heater) for an applied DC voltage of 30V. An

This work was supported by the MEC TEC-2004- 6854-C03 project.
extension of this work would be optimizing the silicon doped and the heater geometry, in order to obtain high levels of power and temperature with sufficiently low voltage levels.

REFERENCES


SINGLE CELL BIOMOLECULAR RECOGNITION BY SILICON INTRACELLULAR CHIPS

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Abstract— Single cell analysis has become a real challenge in cell biology. In this context, the paper reports a proof of concept of the use of micrometer-size silicon chips as single cell intracellular sensor. We have developed a technology and a collecting method for small (< 3 µm) chips production and functionalized chips have been delivered to HeLa cells. The results show that silicon chips can be internalized inside living cells without affecting cell viability and functionalized chips can react with the intracellular medium. These findings provide a starting point for future intracellular silicon NEMS.

Keywords- silicon chips, biomolecular recognition, living cells, HeLa

Introduction

Micron and submicron scale structures are opening new opportunities in cell biology [1]. Several works have shown the use of micro- and nanoparticles (i.e. quantum dots, carbon nanotubes, nanobarcodes, etc...) as interactive systems for single cell analysis [2]. Although their functionality has been demonstrated, their fabrication based on chemical synthesis is a limiting factor in performance and versatility. In contrast, versatile structures as micro- and nanoelectromechanical systems (MEMS, NEMS) are mass-produced using photolithographic processes. Significantly, silicon has been demonstrated to have excellent mechanical and electrical properties and to be chemically functionalized. As a consequence, silicon MEMS have been explored for biomolecular recognition [3] and also for extracellular studies [4]. Recently, Ferrari’s group demonstrated that small porous silicon devices can be used for extracellular drug delivering [5]. We proposed a step further, the internalization of silicon devices by single living cells for intracellular applications.

I. EXPERIMENTAL

Here, we present a basic chip to demonstrate this concept. The fabrication was based on photolithographic processes and MEMS technologies. Silicon Intracellular Chips (ICCs) were fabricated on a 4” silicon wafer, Figure 1.a). First a 1 µm thick silicon oxide layer was deposited on the front-side of the wafer as a sacrificial layer, Figure 1.b). Then, a 0.5 µm thick polysilicon deposition defined the device layer, Figure 1.c). Next, a photolithographic process, Figure 1.d), was combined with polysilicon dry etching to pattern 3 µm wide devices, Figure 1.e). After photoresist removing, the chips were released by a HF sacrificial etching, Figure 1.f). The small chips were suspended by ultrasounds in ethanol and collected by a filter. Figure 1.g) shows the fabricated silicon chips. ICCs were chemically modified in order to study their intracellular sensor capabilities. After surface activation, the chips were immersed (12h, room temperature) in a 1 mM solution of fluorescein diacetate (FDA) isothiocyanate in anhydrous DMF.

II. RESULTS AND DISCUSSION

Internalization of the ICC was tested in a HeLa cell line. Positive results were obtained and the internalization rate was improved by coating the chips with Lipofectamine 2000. HeLa cells with silicon chips were visualized by scanning electron
microscope (SEM), Figure 2.a), and the specific localization of the chips inside the cytoplasm was established by confocal laser scanning microscopy, Figure 2.b). Studies of cell viability also showed that healthy living cells, containing ICCs, were clearly evident after 3 and 7 days in culture.

Figure 2. a) SEM and b) confocal image (white arrows show ICC location) of a HeLa cell with an internalized ICC.

Functionalized chips with fluorescein diacetate (FDA) were delivered to HeLa cells. The interaction of FDA with active cytoplasmic esterases hydrolyzes the acetate groups, producing fluorescein emissions, Figure 3. This result confirms the interaction of the ICC with intracellular biomolecules.

Figure 3. FDA functionalized ICCs (white bar) emits green fluorescence due to the interaction with HeLa cells cytoplasmic esterases.

III. CONCLUSIONS

ICCs can be manufactured at a microscopic scale using standard MEMS technologies, internalized into living cells and used as intracellular sensors without affecting cell viability. Intracellular silicon-based chips will provide endless possibilities for the design of innovative intracellular NEMS for single cell analysis.

ACKNOWLEDGMENT

This study was financed by the Spanish government through the MINAHE 2 project MEC-TEC2005-07996-CO2-01, MINAHE 3 project MEC-TEC2008-06883-CO3-01, the health research project SAF2007-66175 (to EJdlR), and the INTRACELL project CSIC-200550F02418 (to JE, EJdlR & FSB). We also wish to thank the MEC-GICSERV program and the IMB-CNM clean room staff.

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GicServ Program.

External Access to the CNM Clean Room

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Abstract—A summary of the capabilities of the Clean Room of CNM are described altogether with the types of projects that are offered as external use.

Keywords-component; formatting; style; styling; insert (key words)

I. INTRODUCTION

Since 2006, CNM in Barcelona is managing its Clean Room as a Large Scale Facility (ICTS) at national level. This allows, R&D institutions to have access to a variety of technological processes and technologies that can be used in already existing R&D projects. The potential users may apply to the service through a proposal for the specific GICSERV Call of CNM-CSIC If accepted by the ICT external advisory committee the service can be obtained free of charge by the user, through a special funding directly coming from the Spanish Ministry of Science and Innovation. Results of the last calls are provided, altogether with the technological capabilities in order to give maximum diffusion among the Spanish Micro/Nano electronics and Microsystems R&D community.

The deadline of the next GICSERV call is also published.
Silicalite as structural layers for MEMS applications to Chemical Sensors

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Abstract—The aim of this work is preparation and mechanical characterization of well-intergrowth and free-standing c-oriented SIL-1 layer in order to develop chemical resonators with good quality factors and high adsorbent surface. The present results are within the framework of a more ambitious project devoted to the development of highly selective and sensitive pure zeolitic resonators for early detection of explosives taking advantage of the specific and tunable adsorption properties of zeolites combined with their chemical, thermal and mechanical properties.

Keywords- silicalite, structural layers, nanoporous cantilevers, Young modulus, gas sensing

I. INTRODUCTION

Zeolites constitute a family of highly interesting technological materials, on account of their framework structure, with pores of subnanometric size, and their remarkable properties in catalysis and adsorption [1]. Given the interesting properties of zeolite coatings, a significant effort has been carried out to combine the experience gathered in growing zeolite films and the microfabrication methods used in the electronic industry to prepare microstructured devices, especially on Si wafers [2-9] and alumina supports [10].

The final target of our research programme is the development of a highly selective and sensible nanoporous resonator for early detection of explosives. Protecting against explosive-based terrorism can thus only be accomplished by mass deployment of miniature sensors that are sufficiently sensitive and selective [11]. Microcantilever sensing satisfies many requirements for an ideal explosive sensor [12]. The specific and tunable adsorption properties of zeolites combined with their chemical and thermal resistance and viscoelastic properties make them ideal candidates as sensible coatings, as is proven in a recently published review dealing with the application of zeolite-based materials for gas sensing [13]. Indeed, discrete commercial zeolite crystals have already been coated on Si cantilevers for humidity sensing purposes, indoor quality control [14-15] and only advocated as size selective materials to increase the specificity of self-sensing microcantilevers arrays in multicomponent mixtures [16]. The novelty of the approach here described relies on the fact the proposed cantilevers are exclusively constituted by polycrystalline zeolite layers. The promising combination of the intrinsic properties of zeolites with the high mass resolution provided by microcantilevers is exploited for the first time in this work.

The aim of this work is the resonance performance characterization by optical detection of uncalcined and calcined c-oriented silicalite (Sil-1) microcantilevers prepared using standard tools adapted from the microelectronic industry. Several groups [17-18] have developed different techniques (i.e uniaxial compression or nanoindentation testing) for measuring mechanical properties of siliceous zeolite crystals (MFI, FER) on small scales (from 20 to 200 μm in size) in order to evaluate the hardness and the elastic constants. The resonant behaviour of zeolitic membranes has not been previously attempted in the literature. The study of the mechanical properties of free standing policrystalline zeolite membranes carried out will help to make feasible the implementation of zeolites as structural layers in numerous technological areas such as actuators or sensors for MEMS and NEMS applications.

II. FABRICATION PROCESS

In this work c-oriented Sil-1 polycrystalline layers have been synthesized on Si wafers and used as structural layers for micropatterning [19] to develop bulk Sil-1 cantilevers (see Figure 1). To the best of our knowledge this is the first time that a zeolite-only cantilever is proposed.

The fabrication process follows next steps:

a-b-c) Seeding of the polished side of low doped “p” <100> silicon wafer with a dispersion of Sil-1 nanocrystals (100nm particle size) in ethanol (4% wt [20]) by spin-coating [21]. After that, a well intergrowth Sil-1 layer is achieved by secondary hydrothermal growth in a Teflon autoclave. The gel composition and synthesis conditions have been previously described in the literature [22]. Sil-1 membranes around 8±0.5 μm in thickness onto Si wafers have been reproducibly attained. The washing procedure involves several cycles in acetone/2-propanol/DDI water for conditioning before photolithography steps.
Figure 1. Schematic representation of the Sil-1 cantilever fabrication process: a) Starting Si wafer; b) spin coating of Sil-1 nanocrystals; c) hydrothermal synthesis of Sil-1 film; d-e) photolithography process, f) BHF etching of the Sil-1 layers; g) Sil-1 cantilever release by TMAOH anisotropic etching.

d-e) A one step standard photolithography process is carried out using positive resist (AZ9624).

f) Selective buffer HF (Aldrich) etching process is used for the micromachining of SIL-1 structures (10 min, room temperature, followed by cleaning with ultrasonic bath [19]).

g) Finally, a selective silicon anisotropic etching using TMAOH is chosen for Sil-1 microcantilever release (TMAOH 25% vol at 90°C during 3 h. [19]).

Figure 2 shows two identical of the as fabricated Sil-1 microcantilevers 500x120x8 μm (length, width and thickness).

Once the microcantilevers have been fabricated, the organic template used for the membrane growth has to be removed from the microporous zeolite framework. In our case, this activation process has been carried out by calcination at low temperature (200°C) in ozone atmosphere [22-23].

III. EXPERIMENTAL SET-UP

The experimental set-up for the evaluation of the resonant properties is based on piezo-electric excitation and optical detection using laser interferometric methods.

A piezo-electric (PL physik instrumente) vibrating at 300 kHz is glued under the cantilevers chip. A laser beam (He-Ne at 632.8 nm and 15 mW) is guided through 3 mirrors and focalized using a x20 microscope lens onto the tip of the silicalite cantilever. The reflected beam returns across the lens to a beam splitter. 50% of the beam is focalized in a fotodetector (ac-coupled New Focus 1601 high-speed, 30kHz-1GHz), and the other 50% returns to a CCD camera, that is used to record the resonance.

AC fotodetector output and piezo-electric is linked to a Network Analyzer (Agilent 5100A). The interference between the incident beam and the primary one is registered by the detector. The amplitude response of a single cantilever and the phase change is registered. Coventor software was used for resonant mode frequencies assignment.

IV. RESULTS

Table 1 compiles the experimental frequency values obtained. From these data, the intrinsic value of Young Modulus (E) has been calculated by using the following equation:

$$f_0 = \frac{r_n \cdot \frac{t_{c{}ant}}{I_{c{}ant}}} {\left( \frac{E}{\rho} \right)^{\frac{1}{2}}}$$

Eq 1: Relationship between frequency and Young modulus (if it is vertical mode t=thickness, if it is horizontal mode t=width, $\rho = 2000 \text{ kg/m}^3$) and $r_n$ is the coefficient mode dependent.

The Young modulus (E) for well defined as-synthesized SIL-1 polycrystalline cantilevers have been estimated (30.09±5.29GPa). No substantial differences are detected after thermal activation in ozone atmosphere.

Several ethanol vapor detection experiments have been carried on to corroborate the suitability of these cantilevers to be use as gas sensors. Fast response time (less 1 min.) has been observed (figure 3). In comparison with silicon cantilever coated with silicalite, sensor sensitivity to ethanol has been high improved, because whole cantilever is made on sensitive
material (table 2). Sensor sensitivity: (1) silicon cantilever coated with 18.52mg of silicalite; (2) Silicalite cantilever 1000 mm length and (3) silicalite cantilever 400mm length at 2nd vertical mode

<table>
<thead>
<tr>
<th>Length [μm]</th>
<th>Mode</th>
<th>Frequency [kHz]</th>
<th>$E_{Sil}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1st vertical</td>
<td>17.5</td>
<td>27.6</td>
</tr>
<tr>
<td></td>
<td>2nd horizontal</td>
<td>110.6</td>
<td>28.0</td>
</tr>
<tr>
<td>1000</td>
<td>2nd horizontal</td>
<td>97.2</td>
<td>24.6</td>
</tr>
<tr>
<td></td>
<td>2nd vertical</td>
<td>28.6</td>
<td>30.0</td>
</tr>
</tbody>
</table>

**TABLE I.** Mechanical properties of two Sil-1 cantilevers w= 30 μm x t=8 μm (width and thickness).

<table>
<thead>
<tr>
<th>Cantilever</th>
<th>Masa [mg]</th>
<th>Modo &amp; Fn</th>
<th>Sensibilidad [mHz/ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)*Sil+SIL-1</td>
<td>850 +18.52</td>
<td>1st vertical 2.24 KHz</td>
<td>1.3</td>
</tr>
<tr>
<td>(2) SIL-1</td>
<td>0.57</td>
<td>1st vertical 28.5 KHz</td>
<td>17</td>
</tr>
<tr>
<td>(3) SIL-1</td>
<td>0.48</td>
<td>2nd vertical 27.4 KHz</td>
<td>107</td>
</tr>
</tbody>
</table>

**TABLE II.** Sensor sensitivity: (1) silicon cantilever coated with 18.52μg of silicalite; (2) 400 μm length Silicalite cantilever (3) 1000 μm length silicalite cantilever at 2nd vertical mode.

![Ethanol adsorption experiment. 400 μm length silicalite cantilever (1st vertical mode)](image)

**V. CONCLUSIONS**

An integrated microfabrication process for activated Sil-1 microcantilever has been described in this work. From the mechanical properties estimation ($E=30.09\pm5.29\text{GPa}$), the employment of zeolite only resonators as chemical sensors becomes feasible.

**ACKNOWLEDGMENT**

Financial support from Ministry of Science and Innovation (MICINN), and DGA, Spain, is gratefully acknowledged. J. Sesé thanks MICINN, for awarding a Ramón y Cajal researcher contract.

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[14] ...
Layer-by-Layer YSZ potentiometric oxygen gas sensor

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Abstract—The development of a new potentiometric oxygen gas sensor is presented in this work. Thin film technology has been used for the fabrication of a sensor based on the thermoelectric effect. This sensing mechanism consists on an interdigitated electrodes device coated with an Yttria-stabilized Zirconia (YSZ) film by means of the Layer-by-Layer Electrostatic Self Assembly technique. A thermoelectric voltage appears between the two electrodes due to a temperature gradient induced to the YSZ thin film. The magnitude of this voltage depends on the oxygen concentration.

I. INTRODUCTION

In the last 20 years, oxygen sensors have been extensively used in various applications. Major of them are in combustion systems to measure the oxygen content in the exhaust gases to assess the air-to-fuel ratio and minimize air pollution. Other applications include the use in industrial processes, laboratory applications and physiological applications [1]. There are many techniques utilized for the synthesis and fabrication of thick and thin films for chemical sensing. Among others, methods like spin coating, dip coating or screen printing have been already successfully used for the fabrication of oxygen sensors [2]. On the other hand, there are techniques, like the Layer-by-Layer Electrostatic Self Assembly (LbL) method, this method is suitable for the deposition of diverse nanostructured materials (ceramics, semiconductors, metals, biomaterials and others) on many types of substrates of even complex surfaces with convex, concave or even conical shapes [3]. Due to this the LbL method can be successfully used for the synthesis and deposition of sensing thin films. More specifically, we propose here the utilization of the LbL method for the fabrication of a new sensor based on the thermoelectric effect for the measurement of oxygen, in opposition to classic oxygen sensors based on changes of the electrical impedance of YSZ films in presence of oxygen at high temperature [1].

II. EXPERIMENTAL

A. Interdigitated electrode device.

The potentiometric sensor chip consists on a 300 \textmu m thick alumina substrate coated with platinum interdigitated electrodes (250 \textmu m width and spacing) and a platinum resistance detector (RTD) on one side and platinum heater (microhot plate) on the other side. The overall dimensions of the alumina chip are 15mm x 13mm (see Fig. 1).

Figure 1. Schematic overview of the sensing chip

B. Particle and sensing film synthesis.

The sensitive coating was built up using the Layer-by-Layer Electrostatic Self Assembly technique. Firstly, the interdigitated electrodes substrates were cleaned thoroughly. Afterwards they were dipped into a colloidal dispersion of Zirconium (IV) oxide 18% in water stabilized with 1.3% Yttrium oxide (Alfa Aesar) for 2 min and a monolayer of YSZ is adsorbed onto the surface. Later, the substrate is dipped for another 2 min into a poly (sodium-4-styrenesulfonate) PSS (Sigma Aldrich) solution so that another monolayer of PSS is adsorbed. After each dip step the substrate was rinsed in DI water in order to remove the excess of molecules that are not bound and that do not contribute to the monolayer structure. This process is repeated to get the desired number of bilayers, increasing the overall thickness of the coating. Then the device is calcined at 520\textdegree C during 1 hour in a furnace and cooled slowly to room temperature for several hours.

C. Experimental setup.

The experimental setup (see Fig. 2) is formed by three different systems, the gas mixture system, the power supply system and the measurement system. The gas mixture system consists on a panel with different lines connected to three different gas cylinders to transport the gases to a stainless steel test chamber designed at the Public University of Navarra. Each gas line has a mass flow controller (Bronkhorst High-
Tech) that controls the mixture of the gases to get the desired O₂ concentration. The power supply system is a DC power supply (Promax FAC-662B) to feed the heater of the device to reach the operation temperature. Finally, the measurement system is formed by two digital multimeters (Velleman DVM345DI) connected to a computer to measure the voltage generated between the interdigitated electrodes and the resistance of the RTD (to continuously monitor the temperature of the sensor device).

B. Sensor response.

The YSZ film becomes oxygen ion-conductive at high temperatures, from 350°C onwards. A DC voltage of 14V is applied through the heater of the device to reach this temperature and induce a temperature gradient into the YSZ thin film to generate a voltage between the electrodes in presence of oxygen [4]. Fig. 3 shows the response of the sensor at different oxygen concentrations (from 2% to 100%). Fig. 4 shows the dynamic response of the sensor when is submitted to repetitive cycles of 100% Nitrogen and 100% Oxygen.

III. RESULTS AND DISCUSSIONS

A. YSZ thin film.

The structure and morphology of the YSZ sensing film were measured by Atomic Force Microscopy (AFM) and the Field Emission Scanning Electron Microscope (FE-SEM). In AFM measurements, the samples were fabricated onto glass substrates, as far as the roughness of the sintered alumina chips was too high. The AFM analysis revealed that the coating consisted in a continuous and uniform layer of YSZ particles with a overall thickness of 150nm and an average RMS roughness of 49 nm. The FE-SEM images confirmed the existence of a YSZ thin film onto the alumina substrate.

IV. CONCLUSIONS

In this work the Layer-by-Layer Electrostatic Self Assembly method has been studied for the fabrication of a potentiometric oxygen sensor based on an interdigitated electrodes device. The sensor shows a high output range (more than 1 Volt) without electronic amplification in presence of a 100% of oxygen. The sensor response has been analyzed from 2% to 100% oxygen concentration. The response time is of about 60 seconds. A logarithmic relation has been found between the thermoelectric voltage generated and the oxygen concentration. To our knowledge, this is the first time that the LbL method has been used for the fabrication of oxygen sensor based on the thermoelectric effect.

ACKNOWLEDGMENT

This work was supported in part by the Spanish Ministry of Education and Science-FEDER TEC2006-12170/MIC and Gobierno de Navarra Euroinnova Research Grants.

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Single-use microvalves in SU-8 and PCBMEMS technologies for Lab-on-Chip applications

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Abstract—Two novel microfluidic single-use valves for fluid injection and extraction in Lab-on-chip (LOC) applications are presented in this paper. The devices consist in a thin SU-8 membrane crossed by a resistor that withstands a mechanical stress induced by a pressure difference. When the resistor heats up the membrane, the SU-8 fracture strength drastically decreases causing the valve activation. The microvalves have been designed, fabricated using inexpensive SU-8 and Printed Circuit Board technologies, and finally experimentally characterized. The simple fabrication process and the absence of moving mechanical parts have made these designs suitable for large-scale integration in Lab-on-Chip microfluidic platforms.

Keywords: Microvalve, SU-8, PCBMEMS, Microfluidics, LOC

I. INTRODUCTION

During the last two decades, development and fabrication of microfluidic elements have supported many innovative applications in areas like chemistry, biology and medicine [1]. The LOC concept concerns handling, manipulation and analysis of small samples of fluids to realize the functions of a bio-laboratory in a single chip.

Traditional microfluidic devices are fabricated in silicon or glass, but high costs and limited accessibility of silicon processing have driven interest in exploring other materials and technologies [3]. In this respect, the SU-8 is an epoxy-based negative photoresist, whose properties make it a useful and inexpensive alternative [4]. It can be patterned using standard mask processes with very thin films and nearly vertical sidewalls profiles. Another technology that is becoming important in miniaturized fluid components is Printed Circuit Board Microsystems (PCBMEMS), which combines mechanical, electronic and fluidic devices by adding some new steps on common PCB fabrication process [5]. The main advantages lie in the low cost, robustness and ease of integration, making this option really interesting for LOC fabrication.

One of the essential devices of microfluidics in biomedical applications are the valves. Their function consists on driving biological fluids through the microchannels, activating the fluid flow in order to produce an analysis. The valves presented in this paper have been conceived as a part of a microfluidic and electronic PCB platform with microneedles and sensing elements so high integration has been the most important specification taken into account [6], [7].

II. OPERATION PRINCIPLE

The microvalves consist of a thin SU-8 membrane crossed by a resistor element. A pressure difference is fixed between both sides of the membrane in order to cause a mechanical stress over the structure. This stress will produce a breakage on the membrane when an electric current is supplied through the resistor element. The thermal power due to the resistor weakens the membrane, acting as a trigger for the activation. In absence of electric current the membrane will remain as a solid barrier, withstanding the pressure difference between both sides. Therefore, the microvalves actuation is achieved by a combination of mechanical and thermal actions. When the membrane is broken, the air contained in the higher pressure side will flow towards the other side of the membrane in order to reach the equilibrium of pressures, pushing the fluid contained in a reservoir or a microchannel connected to the microvalve.

III. PLANAR DESIGN

An overhead and cross-section view of the planar design is shown in figure 1. Pressure on chamber and microchannel will determine the fluid flow direction, establishing a reversible valve operation mode [8].

Figure 1. Cross-section view (a) and top view (b) of the planar microvalve design.
A. Fabrication Process

The implementation of the planar microvalve has been carried out with a simple fabrication procedure and low-cost materials, as is shown in Figure 2.

![Fabrication Process Flow](image)

B. Experimental Results

The fabricated planar microvalve is shown in figure 3.

![Photograph of the planar microvalve](image)

Several microvalves with different membrane widths (from 40 to 70 µm) were produced and prepared for pressure and temperature assays. An optimal balance between power consumption and pressure required will be necessary to optimize the microvalve operation. Experimental results proved the microvalve functionality, working in a pressure range up to 0.8 MPa and presenting an energy consumption of 0.7 J for less than 3.2 seconds to be open [9].

IV. VERTICAL DESIGN

In a similar manner to the planar design, both chambers are connected by an orifice made in the PCB. Over the orifice a gold wire is bonded. The orifice is covered by the SU-8 membrane that will be melted when the valve will be activated.

Then, the fluid that flowed vertically across the bottom chamber will be collected [10].

![Cross-section view of the vertical microvalve design](image)

A. Fabrication Process

The implementation of the vertical microvalve is detailed in the process flow shown in Figure 3.

![Vertical microvalve fabrication process](image)

B. Experimental Results

An enlarged view of the fabricated vertical microvalve is shown in figure 6.

![Photograph of the vertical microvalve](image)
A series of microvalves has been manufactured varying the thickness of the membrane, from 30 to 100 µm. The activation is optimized in each case changing the pressure and current applied. In the 35 µm membrane design, the valve required 0.4 J for 2 seconds applying a pressure of 0.1MPa.

CONCLUSION

Two single-use microvalves for LOC microfluidic applications have been presented. By means of a hybrid thermal and mechanical actuation principle, low power consumption has been achieved. The main advantages of these devices lie on the simplicity, robustness, great functionality and ease of integration, improving previously reported single-use valves due to its simple fabrication process and low cost based on SU-8 and PCBMEMS technologies.

The devices have been conceived as single components of a microvalve array platform, being a key part of an integrated microfluidic LOC. Valve portability can be improved by adapting a small battery with an activation switch and adding a pressurization extra step in fabrication process. Future works also include integration of microneedles and biochemical sensors to analyze biological substances.

ACKNOWLEDGMENT

The described investigations were carried out within the research project MEDITRONIC granted by the Junta de Andalucía (Spain) (P06-TEC-01561).

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Numerical simulation of a degenerated ZnO diode

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Abstract—In this work we present the development of a 1D numerical simulator for a highly degenerated PN junction. This work presents the required modifications in drift-diffusion equations to simulate this device in large doping level condition. Band-to-band tunnel recombination mechanism is also discussed as it is the most important contribution to the total current.

I. INTRODUCTION

The scaling laws of integrated circuit design require that doping levels have to be increased as the devices are miniaturized [1]. Moreover, in the last years, the fabrication of ferromagnetic semiconductors, such as Mn/Co-doped GaAs or GaN, that permit the manipulation of the electron spin degree of freedom is opening a new route to semiconductor spintronics, where the spin-dependent phenomena becomes dominant in electrical and optical properties. Some basic semiconductor device structures such as PN junctions, light-emitting diodes and resonant-tunnelling diodes have been made of Mn-doped GaAs and Co-doped ZnO [2]. This kind of new ferromagnetic semiconductor are usually degenerate because high carrier concentration is necessary to guarantee a strong interaction between the carrier spin and the spins of the magnetic impurities at high temperatures.

In our work we focus on the numerical simulation of a ferromagnetic PN junction, in order to obtain realistic results of the I–V characteristic and to study the effect of the spin polarization on the diode. The first step is the development of a numerical simulator for a degenerate PN junction using the drift-diffusion formalism. This paper presents the results of the implementation that we have made. It is structured as follows: in section II the drift-diffusion model and the necessary modifications to consider degeneracy are explained, in section III we present the implementation in the simulator of the band to band tunneling processes and in section IV we describe the I–V characteristic obtained using our simulator and summarize the conclusions.

II. TRANSPORT EQUATIONS

The drift-diffusion equations are obtained from the Boltzmann transport equation under several simplifications [3]. Under isothermal conditions the electron the carrier current densities are

\[ J_n = -q_e \mu_n n \nabla \phi_n \]  

\[ J_p = -q_e \mu_p p \nabla \phi_p \]  

\[ \phi_n \text{ and } \phi_p \text{ are the pseudopotentials for electrons and hole, and} \]

\[ \mu_n \text{ and } \mu_p \text{ are the mobilities defined by} \]

\[ \mu_n = q_e \frac{\tau_n}{m_n^*} \]

\[ \text{with } \tau_n \text{ and } m_n^* \text{ are the relaxation time and the effective mass respectively, similar equation can be write for holes. In our case, we are using constant values to the carrier mobilities.} \]

In the degenerate case, the Boltzmann approximation is not valid, therefore, the relation between the quasi-Fermi energies and the carrier concentration is given by the Fermi-Dirac statistics through the Fermi integral \( F_{1/2} \), then

\[ n = N_c F_{1/2}(\eta_n) \]

\[ p = N_c F_{1/2}(\eta_p) \]  

where

\[ \eta_n = \frac{E_{F_n} - E_C}{k_B T} \]

\[ \eta_p = \frac{E_{F_p} - E_C}{k_B T} \]  

The gradient of the carrier concentration can be calculated from equations (4) as it follows

\[ \nabla n = \frac{N_c}{k_B T} F_{1/2}(\eta_n) \nabla \eta_n = \frac{N_c}{k_B T} \frac{\nabla E_{F_n} - \nabla E_C}{k_B T} \]  

where we use that

\[ \frac{d}{d\eta} F_{\nu}(\eta) = F_{\nu-1}(\eta) \]  

Knowing that \( E_{F_n} = -q_e \phi_n \), we have

\[ q_e \nabla \phi_n = -\frac{K_B T}{N_c F_{1/2}(\eta_n)} \nabla n - \nabla E_C \]  

Using the expression for the Fermi pseudopotential in equation (1), the electron current density is

\[ J_n = \mu_n n \left( \frac{K_B T}{N_c F_{1/2}(\eta_n)} \nabla n + n \nabla E_C \right) \]

\[ J_p = \mu_p \left( \frac{F_{1/2}(\eta_p)}{F_{1/2}(\eta_p)} \right) K_B T \nabla p - p \nabla E_V \]  

Following the same steps the hole current density is

Consequently, the current density is related with local electric field in the device (\( \nabla E_C \) and \( \nabla E_V \)) and the gradient of the carrier concentration (\( \nabla n \) and \( \nabla p \)). \( F_{1/2}(\eta_n) \) is a correction factor that takes account of the local degeneration level.
III. TUNNELING CURRENT

The tunneling processes through the forbidden energy band is the most important contribution to the total current in a highly doped PN junction at low applied bias. The basic principles of the band-to-band tunnel processes were well explained by Kane [4]. The tunnel mechanisms are added to the drift-diffusion model as recombination terms in the continuity equations, and we use a non-local model for which takes into account the real spatial transport of charge in this processes. It is based on the work of Ieong et al [5]. The probability that an electron tunnels from the position $u$ to the position $l$ and then recombines with a hole is obtained using WKB approximation

$$
\Gamma_{c\rightarrow v} = \exp \left( -2 \int_{l}^{u} \frac{\kappa_{c}(x, \epsilon) \cdot \kappa_{v}(x, \epsilon)}{\sqrt{\kappa_{c}^{2}(x, \epsilon) + \kappa_{v}^{2}(x, \epsilon)}} \, dx \right), \quad (11)
$$

where $\kappa_{c}$ and $\kappa_{v}$ are the wavenumber vector which contain information about the effective mass and the energy of the carrier that take part in the tunnel process. The local tunnel recombination rate is obtained from equation (11) as

$$
R_{c\rightarrow v}(u, l, \epsilon) = \frac{A_{cv}}{qK_{B}} \times F \times \Gamma_{c\rightarrow v}(r) \times T \times \log \left[ 1 + \exp \left( \frac{E_{F_{p}(l)-\epsilon}}{K_{B}T} \right) \right] \left[ 1 + \exp \left( \frac{E_{F_{p}(u)-\epsilon}}{K_{B}T} \right) \right]^{-1}, \quad (12)
$$

The logarithmic factor acts as a supply function of electrons and holes to participate in the tunnel processes, $T$ is the temperature, $F$ the local electric field and $A_{cv}$ is the effective Richardson constant ($A_{cv} = \sqrt{g_{v}, g_{c}} A_{0}$, where $g_{c}, g_{v}$ is a scaling factor and $A_{0}$ is the Richardson constant).

IV. RESULTS

To analyze the behavior of our implementation, we simulate an asymmetric ZnO PN junction. We choose this material because of the growing interest in using it as N-type ferromagnetic semiconductor to develop optically active devices. We use the following parameters: $E_{g} = 3.37$ eV, $\chi = 4.20$ eV, $\epsilon_{r} = 8.565$, $m_{n}^{*} = 0.24m_{0}$, $m_{p}^{*} = 0.59m_{0}$, $\mu_{n} = 8500$ cm$^{2}$V$^{-1}$s$^{-1}$, $\mu_{p} = 400$ cm$^{2}$V$^{-1}$s$^{-1}$, suitable for ZnO [6]. The chosen doping levels are $N_{d} = 1 \times 10^{20}$ cm$^{-3}$ for the donors in the N-side and $N_{a} = 3 \times 10^{20}$ cm$^{-3}$ for the acceptors in the P-side, in a constant profile for each side. This doping level leads to the typical carrier concentration range in magnetic semiconductors to observe the effect of ferromagnetism at near or over room temperatures.

Figure 1a shows the obtained energy band diagram in equilibrium, where it is possible to see the high degeneration level of the carrier concentration. For this band diagram it is easy to see the high probability of the tunnel recombination processes for electrons in the conduction band with holes in the valence band through the band gap. This component of majority carrier current will be important only for low biases because it is limited by the distance between the valence band edge energy in the massive P region and the conduction band edge energy in the massive N region.

Figure 1b shows the I–V characteristic for low bias where the tunneling current is dominant. It is possible to see how the simulation results follow the Kane prediction that the tunnelling current reaches its maximum around the minimum distance between the Fermi level and the conduction band edge in the massive N region ($\epsilon_n$) and valence band edge in massive P region ($\epsilon_p$), $V_a = 0.25$ V in our case, and then becomes zero when the bias reach a value of ($\epsilon_n + \epsilon_p$)/$e$, $V_a = 0.6$ V in our case, as clearly can be seen in Fig. 1c.

ACKNOWLEDGMENT

This work was supported by Spanish Government (MCYT TIN2007-67537-C03-01), and by Xunta de Galicia (DX-IDIOITIC01CT and INCITE08PXIB206094PR).

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Selective electroplating of gold electrodes inside microfluidic channels for biomedical sensing

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Abstract—Platinum has been electrodeposited over gold microelectrodes embedded into fluidic microchannels. The objective of this work is to increase the sensitivity of sensing electrodes inside a microdevice. The technique enables the selective platinization of the area of the selected electrode inside the channel without affecting the rest of the electrical path.

Keywords: microelectrodes, impedance sensing, platinum black, electroplating, lab-on-a-chip, microfluidics.

I. INTRODUCTION

Microfluidics offers an ideal platform to integrate cell-based assays with electric measurements. The technological advances in microfluidics, microelectronics, electrochemistry, and electrophysiology have greatly inspired the development of microfluidic/electric devices that work with a low number of cells or single cells. The applications of these microfluidic systems range from the detecting of cell culture density to the probing of cellular functions at the single-cell level [1].

A typical problem when trying to miniaturize electrodes for its use in the sensing of liquids is the increased relevance of the electrode-electrolyte impedance (i.e. double layer impedance). The series double layer impedance is inversely proportional to the electrode surface area. Therefore, the downsizing of the electrode area unavoidably increases its impedance value and thus reduces the system sensitivity.

Here we present a method to avoid this limitation by selectively on-chip electroplating the portion of the electrode that is in contact with the fluid and leaving the rest of the electrode path and other surrounding electrodes unaffected. The electroplated metal increases the effective area of the electrode thus reducing the effect of the interfacial impedance.

II. MATERIALS AND METHODS

The chip has a single channel connected to the exterior by two reservoirs. Electrodes are coplanar and perpendicular to the direction of the channel. Ti-Au planar electrodes have been fabricated by standard soft lithography on a glass surface. Channels have been fabricated in polydimethylsiloxane (PDMS) by means of soft lithography [2]. Electrodes are 40 μm wide and 40 μm separated and channels are around 500 μm wide.

Platinization solution was prepared with 100 ml H2O, 0.01g of chloroplatinic acid (Sigma Aldrich) and 1g of lead acetate (Sigma Aldrich) diluted in water [3] and introduced inside the chip via one of the reservoirs. A Keithley 6430 sub-Femtoamp power supply (Keithley Instruments) was used to supply a constant current/voltage between one of the electrodes and a platinum wire inserted in one of the reservoirs as shown in Figure 1.

Electrical Impedance Spectroscopy (EIS) measurements were performed with an Agilent 4294A impedance analyser, with an excitation voltage of 1 V and a frequency range between 40Hz and 110 MHz.

III. RESULTS AND DISCUSSIONS

A. Platinization experiments

When the correct polarization is applied, platinum atoms dissociate from the acid inside the solution and are directed towards the gold surface of the microelectrode (Figure 2). Then, depending on the energy that they carry when arriving to the metal surface, they can stay adsorbed to the surface. This is a random process that can lead to the gold surface completely covered by platinum giving rise to a porous surface that incredibly increases the effective area of the electrode thus reducing the double layer impedance associated to it.

Figure 1: Schematics of the electroplating set-up.

The key parameter governing this process is the current density at the electrode surface. Classical electrodeposition experiments of platinum on large metal electrodes have used current densities around 30 mA/cm2 [4,5]. However, for other experiments with microelectrodes [6-8] electrical current densities have been on the range of 50 to 500 mA/cm2.

During our investigations, we could see that optimal current densities in order to obtain good homogeneous platinum density of the gold electrode area had to be between 10 and 50 mA/cm2 applied for time periods between 10 and 30 seconds.

The results of a platinization experiment are presented in the image of Figure 3. Bright yellow area in the electrodes indicates that the gold surface is visible. The presence of platinum is evidenced by the dark brown. Electrodes 1 and 2 were not electroplated. Electrodes from 3 to 6 experienced 6 cycles of ±
uA (15 mA/cm²) of 10 seconds each step followed by 7 seconds of ultrasound agitation. Finally, a second process of electroplating (6 cycles again) was performed over electrodes 5 and 6 uniquely.

It can be clearly appreciated from Figure 2 how electrodes are selectively platinized only inside the channel limits while outside areas remain invariable. It is also remarkable the differences in appearance between electrodes 1-2 (not electroplated), 3-4 (electroplated once) and 5-6 (two times electroplated).

![Figure 2: Optical microscope images of electroplated electrodes](image)

**Figure 2: Optical microscope images of electroplated electrodes**

**B. EIS measurements: double layer impedance reduction**

In order to confirm the hypothesis of the interfacial impedance reduction, electrical impedance spectroscopy (EIS) measurements were made for each pair of electrodes in the chip. The results for the impedance module between the chip electrodes are presented in Figure 3. It can be clearly seen that the double layer impedance of the electrodes (component of the impedance at low frequencies) is reduced by means of the electroplating process.

Taking as a reference the impedance spectra between electrodes 1 and 2 (plane gold electrodes), the measured double layer impedance (component of the impedance at low frequencies) between electrodes 3 and 4 (1 time platinized) is slightly reduced by a factor close to two. Moreover, after a short ultrasound agitation and a second process of cyclic platinization, the impedance of the electrodes is reduced by a factor around 100 (impedance between electrodes 5 and 6, platinized two times, blue line in Figure 3). Ultrasound agitation cause again that platinum that is not well attached to the surface is extracted from it. This explains the great difference in appearance and impedance measured between electrodes 3-4 and electrodes 5-6.

The incredible reduction on the double layer impedance also brings as a consequence that the resistive response of the system is enlarged. So that, while for gold (plane) electrodes the resistance of the electrolyte can only be “seen” for frequencies between 1 and 10 MHz, for the more platinized electrodes, this frequency range starts around 1-10 KHz.

All these results have been obtained for an electrolyte (NaCl) with a measured conductivity of 1 S/m, which is very close to the conductivity of physiological fluids like PBS (1.6 S/m). In addition, higher and lower conductivities have been also used and we have obtained identical results.

Finally, it is important to emphasize that platinum deposited on electrodes shown in Figure 3 has demonstrated good resistance to small ultrasound agitation (a few seconds) and flushing of fluid at high flow rates (200 ul/min), so that they are suitable for any microfluidic or on-chip application.

**Figure 3: Impedance module versus frequency for electrodes with different levels of platinum electrodeposition.**

**IV. CONCLUSIONS**

We have successfully electroplated gold microelectrodes inside a microfluidic channel. The electroplating is performed once the device has been completely sealed and selectively plates the portion of the electrode inside the channel. Such methodology could be used to improve electrical response on lab-on-a-chip (LOC) devices having dielectrophoresis (DEP) based microorganisms manipulation, or integrating impedance and electrochemical sensors.

For impedance based detection purposes and DEP based manipulation, the increase of the effective area of the electrodes allows to use more conductive buffers, that are more suitable for some cell studies, in tinny electrodes. On the other hand, it also permits the application of frequency signals of the lower spectra allowing to perform impedance and DEP analysis of cells, bacteria, or yeasts, in a broader bandwidth of frequencies. This will ultimately allow a better characterization, manipulation and sorting of them.

In the case of integrated electrochemical biosensors is suitable to increase their sensitivity to the detected analyte.

**ACKNOWLEDGMENT**

We would like to acknowledge Dr. G. Gomila from the Institute for Bioengineering of Catalonia who courteously helped us with the experimental set-up.

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Sensors for dopamine detection based on phthalocyanine and AgNPs layer-by-layer films

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Abstract - An alternative way to produce Layer-by-Layer (LbL) films containing iron phthalocyanine (FePC) in non-aqueous media (chloroform) and silver nanoparticles (AgNPs) is presented. The electrochemical properties of the LbL films were successfully applied in detecting dopamine in KCl aqueous solutions at different concentrations using cyclic voltammetry.

Key words – sensors, LbL films, iron phthalocyanine, dopamine, SERS, cyclic voltammetry.

I. INTRODUCTION

The method of preparing alternating layers was initially proposed by Iler [1] in 1966 for positively and negatively charged colloidal particles. Two decades later, Netzer and Sagiv [2] developed an approach to build up multilayers based on self-association and self-organization through chemical interactions, generally covalent bonds. In the early 1990s, Decher et al [3] reported the preparation of multilayer films through the self-assembly process with the alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces, which was extended in Rubner’s group by Ferreira et al [4] for conjugated polyelectrolytes on charged surfaces, and was extended in Rubner’s group by Cheung et al [5] for conducting polymers. Nowadays, the application of organic thin films as transducer elements in electronic devices has been widely exploited, with the electrostatic Layer-by-Layer (LbL) technique being one of the most powerful tools to produce such films.

However, the conventional LbL method is restricted in many cases to water soluble compounds. Here, an alternative way to produce LbL films containing iron phthalocyanine (FePC) in non-aqueous media (chloroform) is presented. This film fabrication was made possible by exploiting the specific interactions between Fe and NH2 groups from PAH, poly(allylamine hydrochloride) used as the supporting layer, leading to the formation of bilayers structured as (PAH/FePC)n. We have also incorporated silver nanoparticles (AgNPs) in LbL films with (PAH/FePC/AgNP)n trilayers, making it possible to achieve the surface-enhanced Raman scattering (SERS) phenomenon. The molecular architecture of the LbL films was determined through different techniques. The growth was monitored with UV-Vis absorption spectroscopy, their morphology characterized by optical and scanning electron (SEM) microscopes, and their molecular organization determined using FTIR. The electrochemical properties of the LbL films were successfully applied in detecting dopamine in KCl aqueous solutions at different concentrations using cyclic voltammetry. The results confirmed that the LbL films from FePC in non-aqueous media keep their electroactivity, while showing an interesting electrocatalytic effect.

II. EXPERIMENTAL METHOD

The (PAH/FePC)n LbL films were grown from 0.5 mg/mL of PAH (Aldrich) in aqueous solution prepared with ultrapure water (18.2 MΩ·cm) from a Milli-Q system model Simplicity and 0.5 mg/mL of FePC (Aldrich) in chloroform (CHCl3). In addition, (PAH/FePC/AgNP)n LbL films were fabricated using Ag colloidal solution obtained by reducing silver nitrate with sodium citrate following the method proposed by Lee and Meisel [6] in 1982 and used as synthesized. The multilayer LbL films were made by immersing the substrate for 3 min alternately into PAH and FePC solutions in the case of bilayers and PAH, FePC, and Ag colloidal solutions in the case of trilayers. After each deposition step, the films were rinsed with ultrapure water and left drying in air for another 3 minutes. The speed of withdrawal of the substrates was controlled to be 8.5 mm/min using a mechanical dipper. The number of bilayers (or trilayers) and the substrate for each film differed depending on the characterization methods.

Cyclic voltammetry was carried out using an EG&G PARC 263A potentiostat/galvanostat (M270 Software) with a conventional three-electrode cell. The reference electrode was a saturated Ag/AgCl/KCl electrode and the counter electrode was a platinum plate. The LbL films were immersed into 0.1 M KCl aqueous solution with the dopamine (Aldrich) being added at several steps leading to concentrations at 2.0x10⁻⁶, 3.0x10⁻⁶, 6.0x10⁻⁶, 1.0x10⁻⁵, 1.5x10⁻⁵, 2.5x10⁻⁵, 7.5x10⁻⁵, 9.2x10⁻⁵, 1.08x10⁻⁴, 1.25x10⁻⁴, 1.75x10⁻⁴ and 2.75x10⁻⁴ M. The cyclic voltammograms were recorded from –1.0 up to +1.0 V at a scan rate of 100 mV/s, and starting at 0.0 V.
III. RESULTS AND DISCUSSION

The electrochemical catalytic effect of the LbL films was tested towards dopamine. Figure 1 shows the voltammograms recorded using the ITO-modified electrode with the LbL film containing 5 bilayers of PAH/FePc immersed in solutions with different concentrations of dopamine (from 2.0x10^{-6} M up to 2.75x10^{-4} M). The curves are dominated by an anodic peak with maximum at ca. 0.12 V associated with the dopamine oxidation. The intensity of the peak associated with dopamine is higher when using LbL films of PAH/FePc and of PAH/FePc/AgNP deposited in non-aqueous medium. This is consistent with the better electrocatalytic activity shown by the unsubstituted phthalocyanine. The electrocatalytic effect is improved in the presence of AgNPs. Figure 2 shows the linear relationship (r^2=0.983) between the peak current and the dopamine concentration in the range between 2.0x10^{-6} M and 9.7x10^{-5} M. The detection limit calculated from IUPAC (3\sigma criteria) was 0.86x10^{-6} M. The limit of detection and quantification were calculated statistically as follow: LD = k × SB/b, where SB is the standard deviation of the blank, b is the sensitivity of the method (determined as the slope of the calibration curve) and k is a statistical constant (value of 3 for LD is widely accepted) [7] that is consistent with the reported value for LbL films of phthalocyanines [8].

IV. CONCLUSIONS

The LbL technique was successfully applied to produce thin films using FePc in non-aqueous media either as bilayers of (PAH/FePc)_n or as trilayers of (PAH/FePc/AgNP)_n. The micro-Raman and the FTIR data revealed that the interaction between Fe and NH_2 groups of PAH is the main driving force for the growth of the LbL films with FePc in non-aqueous medium. The morphology revealed the presence of FePc aggregates in the LbL film. Although the presence of aggregates at the micrometer scale may suggest a lack of control in the fabrication of the PAH/FePc layers, the linear growth evidenced by UV-Vis absorption data and the FTIR and cyclic voltammetry results demonstrate that the properties are well defined in average leading to reproducible results. Furthermore, the AgNPs are found to physically adsorb onto the FePc layers as isolated or aggregates, thus allowing one to obtain both SERS and SERRS spectra.

The effectiveness of achieving the surface-enhanced phenomenon is demonstrated by enhancement factors of ca 10^4 for SERS and 10^2 for SERRS. The LbL films with bi and trilayers were effectively applied as a proof-of-principle in the detection of dopamine in KCl aqueous solutions down to 6x10^{-6} M using cyclic voltammetry. It is also revealed that the electroactivity of FePc is maintained in the presence of dopamine despite the Fe-NH_2 interaction, for which the FePc aggregates might play a key role. The films deposited in non-aqueous medium display an increased sensitivity towards dopamine and justify their use as catalysts and electrochemical sensors.

ACKNOWLEDGMENT

FAPESP and CAPES (process 118/06) from Brazil and MICINN (PHB2005-0057-PC) from Spain for the financial support.

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A brief overview of the different technological applications studied at the NFP Research Group is presented. Our research field is the use of nanoporous interfaces, in a multiplicity of shapes and textures and to deploy these structures on a variety of surfaces and environments. In particular, applications in microreactors, microsensors and microfuel cells as examples of the improved performance achieved by the outstanding features of nanoporous structures are discussed.

**Colloidal zeolites, zeolite films, polycrystalline layers, microreactors, microsensors, proton-exchange composite micromembranes.**

I. INTRODUCTION

Zeolites constitute a family of highly interesting technological materials, on account of their framework structure, with pores of subnanometric size, and their remarkable properties in catalysis and adsorption [1-2]. In particular, the possibility of hosting different ions, atoms, molecules and clusters in the zeolite structures has opened up numerous opportunities as nanomaterials with advanced properties [3-4]. During the last two decades procedures for the preparation of zeolite coatings as films and membranes on different supports have been developed, opening up new applications in the fields of reaction and separation as shown by several reviews in recent years [e.g., 5-7]. Among the novel applications, the deployment of zeolite films seems highly interesting for microchemical systems [8] (microreactors and membrane microseparators). The molecular recognition functionality of zeolites has been exploited in chemical sensors, where zeolite coatings have been shown to greatly increase the selectivity of reactive [9] and mass sensing devices [10]. Also, the incorporation of highly hydrophilic zeolites (low Si/Al ratio) to proton conductive polymers has also been attempted to improve the performance of electrolyte membranes in HT PEMFC [11].

Given the interesting properties of zeolite coatings, a significant effort has been carried in the NFP Research Group out to combine the experience gathered in growing zeolite films and the fabrication methods used in the electronic industry to prepare microstructured supports, especially on Si substrates. Several works in the mid 1990s [12-13] explored the formation of zeolite films on Si wafers and the possibilities to control crystal orientation. These methods have been expanded and adapted in recent years to produce catalytic zeolite coatings on microchannels and zeolite micromembranes, for use in microreactors and microseparators. In particular, we have reported the formation of continuous zeolite films on microstructured supports yielding unprecedented fluid-solid contact area for reaction applications [14].

In a step further, the fabrication of zeolite-only free standing [15] has allowed us to develop silicalite-only cantilevers exhibits sensitivity values two orders of magnitude lighter than conventional cantilevers modified with individual silicalite nanocrystals [16].

II. EXPERIMENTAL

A. Synthesis of zeolite crystals

Different types of zeolite crystals and deposition methods have been used on the substrates in order to find out the best conditions to prepare homogeneous zeolite layers and at the same time attain a sufficient load of active mass for each particular application.

Colloidal suspensions of MFI (silicalite and ZSM-5), zeolite A (LTA), and zeolite Y (FAU) were created with zeolites prepared according to previously reported methods [17-19], while suspensions of Beta (BEA) and mordenite (MOR) zeolites, among others, were prepared with commercially available zeolites (http://www.zeolyst.com). The zeolites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface analysis (BET).

B. Zeolite Films Preparation

Once the suspension with the desired characteristics had been obtained, the methods explored to prepare layers of zeolites on the different substrates included multiple methods as evaporative deposition, microdropping of zeolite suspensions, covalent bonding of the zeolite crystals and spin coating.
III. RESULTS

A. Zeolite based Microreactors

The creation of a regular microstructure followed by seeded hydrothermal synthesis, producing a nanoporous coating, allows the preparation of microstructured–nanostructured coatings with extremely high values of external interfacial area (upward from 400,000 m²/m³).

B. Zeolite Based Microsensors

Etching processes similar to those used in the microelectronics industry can be used to obtain micropatterns on silicalite (SIL-1) polycrystalline films prepared by seeded hydrothermal synthesis. In particular, wet etching can still be used to create patterns on c-oriented films, and seems especially useful to release freestanding zeolite structures, such as zeolite microcantilevers with a high aspect ratio.

C. Polymer Zeolite Composites for Micro-Fuel Cells

In this work, the feasibility of use of zeolites (LTA and MOR) and zeotype materials as raw materials for solid electrolyte membrane fabrication in DMFC has been assessed. Particularly, the use of ETS-10 and Sn–Umbite as solid electrolytes for high-temperature PEMFCs has been reported. ETS-10 crystals could lead to a promising additive for fuel cell membranes and also act as primary proton conducting material in a fuel cell.

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Contributions to MEMS technology

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Abstract— In this paper the Institute for Applied Microelectronics Information and Communication Systems (IUMA), and MEMS division is presented.

Keywords— Working Line; IUMA; MEMS Divisions

I. INTRODUCTION

The IUMA is a research Institute from university of Las Palmas of Gran Canaria (ULPGC) see figure 1. The root of University Institute of Applied Microelectronics lie in the Applied Microelectronics Research Laboratory, set up in 1988 when it received European funding for its inclusion in the initial group of laboratories of the Eurochip programme. This funding came from the PATMOS European project for researching in microelectronics, and from the Spanish Programme of Microelectronics for setting up and equipping Microelectronics labs in Spain. This lab is associated with the Higher Technical School of Telecommunication Engineering. IUMA has more than 40 experience researcher, more than 100 International Publication, 20 complex ICs, 12 Industrial Equipments, and a lots of SW products.

IUMA aims are:

− Promote the investigation in Microelectronic Science, Technology & Application.
− Worldwide spread of R&D results.
− Cooperation with other Research Centers, Business and Public organisms.
− Boost the training and improvement of specialized docents and researchers in microelectronic.

II. MEMS DIVISION

The MEMS division is recently created division of IUMA, focused on Microelectronic and Microsystems, with more than 10 Highly Experienced Researchers more than 50 international journal, participation in more tan 15 R&D Public and Private Projects.

A. Working line

− MEMS.- Analysis, modeling and optimization of electrostatic Induction Micromachines using Finite Element Methods see figure 2, Mathematical models and Genetic Algorithms.
− Microelectronic.- High Performance Logic Families, Fullcustom & Semicustom design.
− Embedded System Design.

Figure 1 Building of the IUMA

Figure 2 FEM analysis
At the present MEMS division IUMA prepares to face one of their most promising research lines in the medium term.

Building on previous work on Electrostatic Induction Micro-motors has been done in the past three years, IUMA prepares to take a step further.

With such work IUMA researchers have acquired some knowledge enabling them to contribute to various publications, and thereby lay the basis for going into their new lines of research.

After the study of micromachines, having used tools like Genetic Algorithms (GA’s) and Finite Element Analysis (FEA), the research division of IUMA MEM’s are prepared to continue on a new line of research, the micro-switches.

Based in the MEM’s, the micro-switches technology are devices that combine mechanical and electrical concepts more traditional with the new concepts of nanofabrication and nanotechnology.

The beginning of this new stage is in turn supported by the inclusion of the Project on Snap IUMA in aerospace applications program of research grants R & D sponsored by Canary Agency Contract Research & Innovation Information Society (ACIIISI).

The ACIIISI is a governmental establishment, under the Government of the Canaries, which is responsible for promoting research and development of new technologies in education and business Canarian society.

In order to obtain this objectives handles bi-and tri aid projects with high technological value of which the MEMS division of IUMA recently has been receiving funding and will shortly begin run, anticipating a period of two years to obtain the first results in the production of microdevices.

To carry out the project of the MEM’s division added to their studies already completed, new input gathered for future doctoral thesis will be conducted in the Department, and will be conducive to the production of micro-switches.

ACKNOWLEDGMENT
The authors gratefully acknowledge the collaboration of the MEMS Division of IUMA (Institute for Applied Microelectronics) at the University of Las Palmas de Gran Canaria, Spain.

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A Monolithic HTCC & LTCC Ceramic Technology for Embedded RadioFrequency Circuitry, Gas Sensing and Microfluidics

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Abstract—A complete microceramic technology based in high & low temperature cofired ceramics (HTCC & LTCC) is presented. The reliability of technical processes is shown. This technology is applied to RF circuitry, nanosensing and microfluidics, as example of the wide potential of ceramic microtechnology.

HTCC, LTCC, microceramic, RF, nanosensing, microfluidics

I. HTCC & LTCC TECHNOLOGY

For many applications ceramics become interesting. The thermal resistance, chemical stability and interesting dielectric properties suggest the use of ceramic devices, structures or substrates for applications such as microfluidics, sensors, radio-frequency, automotive electronics, fuel cells …

Figure 1. Technology procedure from tape casting to firing.

Different approaches have succeeded for developing these devices. Monolithic ceramic technology based on tape casting and cofiring of stacked tapes. This feature allows 3D design and together with screen-printing makes this technology suitable for electronics, sensing and microfluidic applications, and its combination in the same system. Figure 1 summarizes the technology procedure [1-2].

Current status of the technology is quite advanced and is being applied in new promising fields like solar cells [2]. In fact the roughness of cofired ceramic surfaces has been reduced in the last times, figure 2 (Ra<100nm).

Several materials can be used as ceramic. While Al2O3, YSZ or AlN are used for HTCC, a mixture of glass and ceramic is used in LTTC. Usually HTCC tapes should be developed starting from ceramic powders while LTCC tapes are commercially available (e.g. Ferro or DuPont).

II. RF CIRCUITRY

In the recent times, the use of low temperature cofired tapes is common in RF electronics due to desirable low shrinkage of the embedded electronic circuit and ceramic holder. Besides high dielectric performances of the ceramic allow to work up to several tens of GHz [3].

Figure 2. AFM inspection of ceramic surface. Roughness is less than 100 nm

Figure 3. Experimental dielectric properties of the sintered LTCC tape.
In our case, LTCC substrates were first characterized obtaining interesting results of loss tangent and dielectric constant for RF applications, see figure 3.

![Image](image.png)

**Figure 4.** Top view of a symmetric inductor fabricated on LTCC substrate, as reference the device is 4x4mm and 150 µm-thick each arm

As shown in figure 4, passive electronics can be printed in LTCC tapes, either top layer, buried or interconnecting different layers. This embedded passive circuitry can easily complemented by active chips bonded by flip-chip.

![Image](image.png)

**Figure 5.** Electrical response of the LTCC inductor

The electrical results indicates high quality factors working at frequencies up to several GHz.

IIII. GAS SENSING

One of the most attractive features of ceramic microtechnology is the easiness of 3-D structuration, starting from 2-D tapes and monolithically stacking. These posibilities suggest to be used as micromechanics in silicon. In fact, low thermal mass systems can be developed.

In gas sensing materials should be heated up to ~200°C. Old sensors made with thick film technology require up to 500mW to be heated whereas micromechanised silicon hot-plates just 10 mW. The use of microceramics is about 100 mW for our designs. Despite highest consumption that silicion, microceramics robust design is much more indicated in harsh environment like car exhaust or boiler pipes [4-5], see figure 6.

![Image](image.png)

**Figure 6.** Microsensors in ceramic technology. Sensor are 2x2 mm.

IV. CHANNELS, CAVITIES & MICROFLUIDICS

Finally, the use of a monolithic technology combined with smart sacrificial materials allows obtaining channels, cavities and the whole development of microfluidics, suitable for many applications.

![Image](image.png)

**Figure 7.** Scheme of a capacitive ceramic sensor. Inset depicts a real sensor.

As shown in figure 7, capacitive pressure sensors where developed. These sensors requires for a small gap cavity (~10µm). In the next future microfluidic systems will be developed for chromatographic applications.

ACKNOWLEDGMENT

European, Spanish and Catalan Governments are acknowledged for its support in several projects.

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A new design of high precision solar microsensor for satellite applications

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Abstract—This paper shows the design of a miniaturized two-axis sun sensor for satellite attitude control. The high precision will be obtained by the subdivision of field of view (FOV). A sun FOV of ±60° and a resolution of 0.1° will be expected.

Keywords- MEMS, photodiodes, sensor

I. INTRODUCTION

A solar sensor is a very common device used in an attitude control of satellites [1]. The accurate relative position in the space is obtained from the incidence angle measurement of the sun light beam [2]. The starting point of the work shown is this paper was the design, fabrication and characterization of a miniaturized sun sensor for satellite applications by the Universidad de Sevilla (US) and the Universidad Politécnica de Cataluña (UPC) [3]. This sensor combines MEMS and microelectronics technologies with a baseline crystalline silicon solar cell fabrication process, leading to a small area device (<1 cm²), low weight, cost and power consumption. Mechanical, electrical and thermal performance of the sensor device were been tested. The sensor device has been mounted in the Spanish nano satellite NANOSAT-1B, which has been launched in July 2009. Fig. 1 shows the structure of the MEMS for each axis.

Figure 1: One axe sun sensor structure.

Two photodiodes have been manufactured in a silicon p-doped bulk. A cover glass with an upper window allows the sun rays reach the photodiodes and generate a current in each one. From the currents ratio we can obtain the incidence angle of the incoming ray. Fig. 2 shows the encapsulated device, in which the aluminum shell plays an important role in order to protect it against dangerous radiations.

Figure 2: Sun sensor device for satellite application.

II. SENSOR DESCRIPTION

In order to increase the accuracy of measurement is very important to maintain high gain factor without harming FOV and to reduce quantification error in AD converters. A way to solve these two assumptions is using the subdivision of the FOV en N sub regions, as shown in Fig. 3, using in this case five sub regions of Θ grades. In each sub region, the angle for one axis is obtained using two photodiodes, being necessary a total of N+1 photodiodes in order to cover all the field of view (see Fig. 4).

Figure 3.

Figure 4 Multicell design of high precision sun sensor.
Given the illuminated areas of the active photodiodes in one subregion (see Fig. 5) it is possible to determine the angle of incidence using (1).

\[ R_j(\theta_j) = \frac{I_{ph,j} - I_{ph,j-1}}{I_{ph,j} + I_{ph,j-1}} = \frac{A_j(\theta_j) - A_{j-1}(\theta_j)}{A_j(\theta_j) + A_{j-1}(\theta_j)} = \frac{L_j(\theta_j) - L_{j-1}(\theta_j)}{L_j(\theta_j) + L_{j-1}(\theta_j)} \]

Where \( L_j \cdot W \) and \( L_{j-1} \cdot W \) are the illuminated area of the photodiodes \( j \) and \( j-1 \), respectively. The cover glass with the window have to be carefully designed and manufactured to allow the sun rays reach two photodiodes in every time without any disturbances to other ones. Additionally, a lineal or angle mismatch between cover glass and silicon dice, estimated in 20 \( \mu \)m, increases error measurement.

III. SENSOR FABRICATION

New design has meant an improvement in sun sensor properties. However, due to technology restrictions, some parameters, like dimensions and precision, are very limited and can be improved [4]. In order to achieve better properties in the sun sensor several designs will be made. Several structures and technological parameter changes are proposed to test their influences in sensor performance:

A. Oxide Layers

Two different designs, with and without an oxide layer on top of the photodiodes will be manufactured, in order to study the effects of this layer in the current photo-generation.

B. Number of photodiodes per axis

Changing the number of photodiodes, and therefore the number of subdivisions of the FOV will make possible to study the signal-noise ratio in function of the size of the photodiode, and obtain an optimum number of them.

C. Gap size between photodiodes

The gap size between photodiodes is a non-doped region, in which the current photo-generation is practically zero, leading to a lack of information about the light beam, but is necessary in order to define and separate the signal from two adjacent photodiodes. Several designs will be made, changing the gap size in order to get an optimum.

D. Flip-chip technology

Flip-chip technology will be used to link cover glass and silicon dice. Error due to align mismatching will be decrease to several microns. Additionally, flip-chip technology allows including sun sensor dice in a MCM solution where signal processing modules may be included. This objective is very appreciated in order to decrease the total size of sun sensor- auxiliary electronic solution in satellite applications.

As result, a layout with a matrix of different designs will be obtained. This layout will be repeated all over the wafer, in order to study the repeatability. A dice of 10 mm2 for each sensor are expected, representing a quarter the size of the actual chip. A 500 \( \mu \)m thick boron-silicate wafer will be used to design and manufacture the cover glass-window structure with flip-chip technology.

The chip will be manufactured at the facilities of the Centro Nacional de Microelectrónica (CNM), located in Barcelona, at the end of 2009.

IV. CONCLUSIONS

We have presented the design of a high precision solar sensor. Small size and low power consumption has been the principal objectives. For this reason new design has been proposed. However, a set of prototypes will be manufactured to evaluate several parameter influences in sun sensor performance. Once the designs will be tested and validated, a future work could be the integration of the sensor and the auxiliary circuits of signal adaptation in the same bulk, leading to a smaller final device than actual.

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A Self-Calibration Multisensor Interface for AmI WSN Applications

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Abstract—The use of smart sensors in wireless sensor networks is expensive, requiring applying low-cost analogue sensors. This paper presents an interface for analogue sensors designed to adapt their output, optimizing the sensor span. The proposed interface includes both electronic and software elements, and components that let self-calibration to compensate undesired effects in the electronics.

I. INTRODUCTION

The recent advances in mobile communications, have made become a reality the use of low-cost low-power sensor networks in widely diverse environments, which interact by means of wireless communication systems. They offer a broad range of innovative applications [1], such as environmental monitoring, military sensor networks, healthcare applications, forest fires detection, etc.

The goal of the present work is the design and test of a versatile sensor interface able to transform the voltage obtained from a set of analogue sensors placed on a sensor node or mote to a digital code, related to the value of the sensor measurement value. The proposed system is composed of both hardware and software parts.

II. INTERFACE DESCRIPTION

The proposed sensor interface transforms the voltage provided by different sensors with different output ranges to a pulse signal which frequency will depend proportionally on the input voltage. The conversion of the sensor signal to a frequency value will bear much less sensitivity to interferences. In addition, the quasi-digital signal provided by the voltage-to-frequency circuit can be read by a microcontroller using a digital input-output port, saving the more limited analogue inputs. In order to achieve the best performance in the conversion to digital values of the frequency signal, it is necessary to convert the different sensor output ranges into the same frequency range.

A. Electronic interface

Figure 1 show the schematic of the proposed electronic interface. The circuit mainly consists of two successive stages: a programmable voltage adapter circuit that converts the sensor output range to a common voltage range from 0 to 3 V, equal to the supply voltage, and a voltage to frequency conversion circuit. The programmable voltage adapter (surrounded with a dotted line in Fig. 1) fit the gain and the offset voltage, to obtain the maximum voltage resolution.

The voltage at the output of OA2 is described by the following equation

\[ V_{out} = A_{LC} \cdot V_m - (A_{LC} - 1) \cdot V_{offset} + A_{LC} \cdot \left(1 - \frac{R_{WH}^2}{R_{WL}^2}\right) \]  \( (1) \)

In this equation, \( R_{WH} \) and \( R_{WL} \) are the resistance values programmed in the digital potentiometer \( R_{2p} \) from terminals W to H and W to L respectively.

The offset voltage \( V_{offset} \) added to the sensor signal is given by the simple equation of a voltage divisor made with \( R_{1p} \):

\[ V_{offset} = \frac{R_{WH}}{R_{1p}} \cdot V_{cc} \]  \( (2) \)

The second conditioning block consists of a voltage-controlled oscillator (VCO), providing a signal which frequency depends on the 1MHz clock frequency given to the VCO from the microcontroller (CLKIN, Fig. 1), and the supply voltage \( V_{cc} \) (3 V in our case).

B. Software interface

A microcontroller controls the measurement process. It is programmed to select the input of the analog multiplexer (Fig. 1) selecting the sensor (S1, ..., Sn) to be conditioned. Depending on the sensor characteristics, the digital potentiometers \( R_{1p} \) and \( R_{2p} \) are properly programmed, ensuring a suitable input range to the VCO to cover the full frequency output span.

The frequency to digital value conversion is performed using the classical Direct Counting Method (DCM) [2]. This

This work was supported in part by MICINN (RYC-2008-03185, PET2007-00336, PET2006-0221 and TEC2009-09175), DGA-La Caixa (GA-LC-039/2008, GA-LC-033/2009) and DGA (PI 113/09).
method counts the number of pulses \( (N_x) \) of a signal of unknown period \( (T_X) \) in a temporal window defined by \( n \) periods of a signal of known frequency \( (f_0) \).

\[
N_X = n \cdot \frac{T_0}{T_X} \implies f_X = \frac{N_X}{n \cdot T_0}
\]  

(4)

where \( T_0 \) is the period of the known signal and \( f_X \) is the unknown frequency. The bigger is \( n \), the more accuracy is achieved, but at the cost of a larger calculus time. In our case, using a signal of period \( T_0 = 2.5 \times 10^{-7} \) (4 MHz), \( n = 65535 \) provides a suitable tradeoff between accuracy (more than 12 bits) and operation time (16 ms).

\[
F_{OUT} = 0.1 \cdot f_{in} + 0.8 \cdot f_{in} \left( \frac{255 \cdot V_{in}}{dig_2 \cdot V_{ref}} + \frac{dig_1 \cdot dig_2}{255} \right)
\]

(5)

Where \( dig_1 \) and \( dig_2 \) are the digital values programmed into the potentiometers R1p and R2p. Calibration is performed in several steps:

- First, input voltage is set to a known value. For this, the electronic interface includes a low-resolution serial DAC (Fig. 1).
- Digital potentiometer \( dig_1 \) is set to 0. Thereby, the frequency of the input signal to the microcontroller depends only on the value of \( dig_2 \).
- The microcontroller sweeps the word range that can be programmed in \( dig_2 \).
- For each value programmed in \( dig_2 \), the system has the theoretical and measured frequency values, thus allowing finding out the relation between the calculated and real value that must be programmed on the potentiometer. Fig. 2 shows the results achieved in a calibration process for \( dig_2 \).

- Once \( dig_2 \) has been calibrated, its register is set to an arbitrary constant value and \( V_{in} \) is set to 0 V, limiting the frequency dependence to the value stored in \( dig_2 \). Note that in this case, maximum and minimum frequency values are limited to the value stored in \( dig_2 \).

![Figure 1: Electronic sensor interface](image)

**III. SELF-CALIBRATION**

Ageing, component replacement or environmental effects can change the behavior of the electronic components. In order to reduce these effects, the proposed interface includes a self-calibration system which performs the appropriate compensation re-calculating the proper potentiometer values. Using potentiometers with 256 programmable taps, the relation with output frequency is

\[
F_{OUT} = 0.1 \cdot f_{in} + 0.8 \cdot f_{in} \left( \frac{255 \cdot V_{in}}{dig_2 \cdot V_{ref}} + \frac{dig_1 \cdot dig_2}{255} \right)
\]

(5)

Where \( dig_1 \) and \( dig_2 \) are the digital values programmed into the potentiometers R1p and R2p. Calibration is performed in several steps:

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- The microcontroller sweeps the word range that can be programmed in \( dig_2 \).
- For each value programmed in \( dig_2 \), the system has the theoretical and measured frequency values, thus allowing finding out the relation between the calculated and real

![Figure 2: Theoretical (continuous line) and measured (dashed line) frequencies for several values of \( dig_2 \)](image)

**IV. APPLICATION**

Frequency values (right) corresponds to the microcontroller readings performed using the DCM algorithm. As we can see, this frequency curve follows the sensor output practically along the full span.

![Figure 3: Hall linear distance sensor behavior compared to the frequency calculated by the microcontroller.](image)

**V. CONCLUSIONS**

This paper presents a conditioning interface for low-cost analogue sensors. By properly programming the interface electronics, the system takes advantage of the full sensor span. The software interface allows converting the quasi-digital signal provided by the electronics to a digital value, achieving accuracy values higher than 12 bits. The system presents some calibration facilities that allow compensating effects of age, non-idealities or environment, keeping the accuracy constant.

**REFERENCES**

Nanopatterning of ultra-thin HfO$_2$ layers for next-generation III-V MOSFETs

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Scaling CMOS technology to and below 22 nm in the next decade will require the introduction of III-V semiconductors with higher electron mobility than Si in the channel of the field effect transistor (FET) in combination with high-$k$ dielectrics as gate oxides. One of the many challenges that needs to be addressed before this goal can be achieved is the development of an appropriate etching process to pattern the high-$k$ gate oxide at the nanoscale that provides high etch selectivity with respect to the III-V channel material at controllable etch rates, vertical etch walls, and residue-free drain/source areas.

We have developed a new process to nanostructure HfO$_2$ thin films (~10 nm) on GaAs(001) substrates by electron beam lithography (EBL) and inductively coupled plasma reactive ion etching (ICP-RIE) with potential application to III-V field effect transistors. After electron beam assisted deposition of the dielectric layer, a pattern consisting of mesas and stripes of variable surface area separated by 100-300 nm-wide open areas and oriented along various crystallographic directions was transferred by EBL onto the PMMA-masked samples. Subsequently, ICP-RIE of the HfO$_2$ thin films was carried out in a SF$_6$/Ar+ gas mixture at a rate of ~15 nm/min. Characterization of the HfO$_2$/GaAs nanostructured samples by atomic force microscopy (AFM), high-resolution scanning electron microscopy (HRSEM), energy-dispersive X-ray spectroscopy microanalysis (EDX) and transmission electron microscopy (TEM) has shown the formation of well defined HfO$_2$B2B nanopatterns with anisotropic profiles and lateral etched dimensions as low as ~50 nm, in addition to atomically smooth and residue-free GaAs etched surfaces.
A New Digitally – Programmable CMOS Voltage-to-Frequency Converter for Wireless Sensor Networks

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Abstract— This paper presents a new digitally – programmable CMOS voltage-to-frequency converter (VFC) with differential signal processing. It also includes a comparison of the conventional CMOS VFC with single voltage entry. The proposed VFC, designed in a 0.35 \( \mu \)m CMOS technology supplied at 3 V, obtains high performance characteristics: differential entry, high dynamic range, high linearity, low power and digitally programmable gain.

I. INTRODUCTION

Wireless sensor networks (WSN) constitute, without doubt, a key technology for the future because of their broad spectrum of potential applications, such as industrial process control, home automation (domotics), health monitoring, pollutant detection or habitat monitoring [1, 2].

Within the field of sensing, today’s market is advanced towards the so called smart sensors, i.e., integrated intelligent sensor systems that contain on a single chip microsensors (or microsensor arrays) next to all the related sensor electronics for the signal conditioning, processing and conversion necessary to interface the microcontroller [3].

![Smart sensor: (a) conventional set-up and (b) set-up using V/F converter](image)

Figure 1. Smart sensor: (a) conventional set-up and (b) set-up using V/F converter with A/D conversion implemented in the microcontroller.

In conventional systems, as shown in Fig. 1(a), the sensor signal is converted to the voltage domain and then digitized by means of a standard A/D. Alternatively, as shown in Fig. 1(b), quasi-digital smart sensors provide a frequency (time) output signal suitable to be directly interfaced to the microcontroller, which performs the A/D conversion using its internal timers. This simple and low-cost approach offers several advantages, the most noteworthy being high noise immunity, ease of transmission, wide dynamic range and high accuracy of the frequency to code conversion.

This paper presents the comparative of the conventional CMOS VFC (Fig. 2) and a new approach which linearly converts the differential sensed voltage into frequency. It achieves low-power and high performance, therefore fitting in the low-cost, high performance and low-power WSN market.

![Conventional CMOS VFC structure](image)

Figure 2. Conventional CMOS VFC structure.

II. NEW DIGITALLY PROGRAMMABLE CMOS VOLTAGE-TO-FREQUENCY CONVERTER

A. Principle of Operation

The basic scheme of the proposed CMOS voltage to frequency converter (VFC) is shown in Fig. 3.

![VFC’s blocks: (a) sensor, (b) adaptator, (c) programmable gain V/I, (d) differential integrator, (e) analog Schmitt - Trigger](image)

Figure 3. VFC’s blocks: (a) sensor, (b) adaptator, (c) programmable gain V/I, (d) differential integrator, (e) analog Schmitt - Trigger.

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The differential input voltage $V_d$ from the adapter is first converted into a differential current signal by a V-to-I converter, whose magnitude depends on a digital word that sets the gain stage. This current alternately charges and discharges the capacitors $C$ between the limits $V_L$ and $V_H$ of a Schmitt – Trigger, which generates the control signals, $D$ and NOT ($D$), related to the comparison results $V_{CL}$, $V_{CH}$. In this way, a repeated charge and discharge loop is built, with a frequency of oscillation $f_{out}$ given by

$$f_{out} = A \frac{G(V_o^+ - V_o^-)}{C(V_H - V_L)}$$

where $A$ denotes a technological constant.

B. Simulation results and comparative analysis

Conventional and proposed VFCs have been designed in a 0.35 $\mu$m CMOS technology, with single 3 V supply. Simulations have been done using Spectre with a BSIM3v3.2 level 53 transistor model for the AMS 0.35 $\mu$m CMOS technology.

The frequency outputs vs. voltage entry for different temperatures in the new CMOS structure are shown in Fig. 4.

![Figure 4: Frequency output vs. voltage entry for different temperatures in single input mode.](image)

The structure exhibits a high linearity output frequency and a low dependence drift with temperature, less than the classical CMOS VFC presents (Fig 5).

![Figure 5: Frequency output vs. Voltage entry for different temperatures for 1 V entry voltage.](image)

In addition, the new CMOS VFC has also a higher immunity to variations in voltage supply (Fig. 6).

![Figure 6: Frequency output vs. Voltage Supply](image)

III. CONCLUSIONS

A new voltage to frequency converter structure has been presented focusing on the present day increasing demand for low-cost, high performance, low-power interface electronics targeting wireless sensor networks applications. This new CMOS VFC structure increase the classical one benefits:

- Single or differential signal processing.
- Higher linearity than the conventional CMOS structure.
- Similar power consumption.
- Digitally programmable frequency gain.
- Lower temperature coefficient.
- Higher immunity to delay effects (no switches are used).
- Higher immunity to variations in supply voltage.
- Reduced dependency on technological process variations.

ACKNOWLEDGEMENTS

This work has been partially supported by MICINN (PET2007-00336, PET2008-0021, TEC2009-09175, RYC-2008-03185) and DGA (PI113/2009)

REFERENCES

Preparation of single-walled carbon nanotube buckypapers for chemical sensors

A. Ansón-Casaos, J.M. González-Domínguez, E. Terrado, M.T. Martínez

The electrical and textural properties of single-walled carbon nanotube buckypapers were tunned through chemical functionalization processes.

Single-walled carbon nanotubes (SWCNTs) were covalently functionalized with three different chemical groups: Carboxylic acids (-COOH), benzylamine (-Ph-CH$_2$-NH$_2$), and perfluoroctylaniline (-Ph-(CF$_2$)$_7$-CF$_3$). Functionalized SWCNTs were dispersed in water or dimethylformamide (DMF) by sonication treatments without the addition of surfactants or polymers. Carbon nanotube sheets (buckypapers) were prepared by vacuum filtration of the functionalized SWCNT dispersions (Fig. 1).

![Fig. 1. Buckypaper obtained by direct filtration of an aqueous solution of purified SWCNT-COOH.](image)

The electrical conductivity, textural properties, and processability of the functionalized buckypapers were studied in terms of SWCNT purity, functionalization, and assembling conditions. Carboxylated buckypapers demonstrated very low specific surface areas (< 1 m$^2$/g) and roughness factor (Ra= 14 nm), while aminated and fluorinated buckypapers exhibited roughness factors of around 70 nm and specific surface areas of 160-180 m$^2$/g.

Electrical conductivity for carboxylated buckypapers was higher than for as-grown SWCNTs, but for aminated and fluorinated SWCNTs it was lower than for as-grown SWCNTs (Table 1). This could be interpreted as a chemical inhibition of metallic SWCNTs due to the specificity of the diazonium salts reaction used to prepare the aminated and fluorinated SWCNTs. The utilization of high purity as-grown SWCNTs positively influenced the mechanical characteristics and the electrical conductivity of functionalized buckypapers.

<table>
<thead>
<tr>
<th>Buckypaper</th>
<th>Initial NIR purity</th>
<th>Thickness [cm]</th>
<th>$\sigma$ [S/cm]</th>
<th>$R_s$ [Ω/□]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purified SWCNT-COOH</td>
<td>45-50%</td>
<td>0.003</td>
<td>10.8</td>
<td>30.8</td>
</tr>
<tr>
<td>SWCNT (DMF)</td>
<td>25-30%</td>
<td>0.011</td>
<td>1.69</td>
<td>53.7</td>
</tr>
<tr>
<td>SWCNT (DMF)</td>
<td>45-50%</td>
<td>0.007</td>
<td>3.04</td>
<td>47.0</td>
</tr>
<tr>
<td>SWCNT-Ph-CH$_2$-NH$_2$</td>
<td>25-30%</td>
<td>0.008</td>
<td>0.30</td>
<td>413</td>
</tr>
<tr>
<td>SWCNT-Ph-CH$_2$-NH$_2$</td>
<td>45-50%</td>
<td>0.007</td>
<td>2.17</td>
<td>66.8</td>
</tr>
<tr>
<td>SWCNT-Ph-(CF$_2$)$_7$-CF$_3$</td>
<td>25-30%</td>
<td>0.007</td>
<td>0.08</td>
<td>1686</td>
</tr>
<tr>
<td>SWCNT-Ph-(CF$_2$)$_7$-CF$_3$</td>
<td>45-50%</td>
<td>0.009</td>
<td>0.16</td>
<td>698</td>
</tr>
</tbody>
</table>

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J.M. González-Domínguez, E. Terrado, and M.T. Martínez are with Instituto de Carboquímica (CSIC), Miguel Luesma 4, 50018 Zaragoza, Spain.
Abstract: Transistor array based on carbon nanotubes was used to detect DNA hybridization. A new approach for attaching single DNA sequence to the nanotubes was developed. The polymer poly(methylmethacrylate)$_{0.6}$-co-poly(ethylene glycol)methacrylate$_{0.15}$-co-N-succinimidyl methacrylate$_{0.25}$ was synthesized and bonded non-covalently to the nanotube. Aminated single-strand DNA was then attached covalently. After hybridization, statistically significant changes were observed in key transistor parameters. Hybridized DNA traps both electrons and holes, possibly caused by the charge-trapping nature of the base pairs.

We present a methodology [1] for avoiding non-specific DNA adsorption on CNTs, providing, at the same time, a stable binding for DNA probes through robust amide linkages. In our method, the DNA probes are covalently bonded to a polymer that is anchored non-covalently to the CNT walls. We report and analyze the changes of the electrical CNTFET characteristics upon interaction with the chemicals used for binding the DNA and upon hybridization. The hybridization is unequivocally detected, upon a statistical treatment of the electrical data from a large array of devices.

A large array of back-gated carbon nanotube devices are fabricated using conventional microfabrication techniques. Palladium was used as the contact metal, and the device channel length is about 2µm, set by the gap length between the source and drain electrode. There are a total of 896 devices laid out on an 1 cm$^2$ chip. The devices were characterized using the Electroglas 2001X automatic probing station in ambient conditions. Figure 1 shows a typical device.

Figure 1.- Schematic diagram of the CNTFET.

The electrical parameters analyzed show statistically significant changes. $I_p$ distribution decreases and $I_n$ distribution is skewed towards smaller values. This reflects an increase in the density of charge traps. The shift of $V_{tp}$ to more negative values for the forward sweep indicates electron traps, whereas the shift to more positive values for the reverse sweep is evidence of hole traps. Most significantly, there is a very large increase in the hysteresis in the $I_d$-$V_{g}$ sweeps following DNA hybridization.

DNA hybridization produced changes statistically significant in key device parameters, as well as important changes in the threshold voltages reflecting the charge trapping character of the hybridized DNA. Through these observations it has been possible to detect the charge transfer inherent to the hybridization reaction.

REFERENCES