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HIGH PRECISION GAS SENSORS BUILT WITH CERAMIC NANOFILMS

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Resumen

Semiconductores como el SnO_2 (puros o dopados), han sido intensamente utilizados para construir sensores de gases de película gruesa de tipo resistivo que permitan detectar gases tóxicos o combustibles: NO_x, SO_2, CO, H_2, CH_4 o VOCs (Volatile Organic Compounds). Los sensores convencionales basados en SnO_2 microcristalino resultan interesantes debido a su alta sensibilidad y a su temperatura de operación (T_{op}) relativamente baja (350-450)ºC. Los autores han probado que la sensibilidad de varios de los sensores, construidos en el DEINSO-CITEDEF, aumenta en (30-35)% y la T_{op} disminuye de (350-450)ºC a un rango de (180-220)ºC si el SnO_2 microcristalino convencional es reemplazado por SnO_2 nanocristalino para la construcción de los dispositivos. En consecuencia, en los últimos años, se han sintetizado polvos nanocristalinos, con una alta relación [superficie/volumen] y se han empleado con mejoras considerables en los dispositivos. Los sensores de tipo resistivo operan en presencia de oxígeno y se han estudiado los mecanismos de sensado para los casos de SnO_2 micro- y nanocristalino. El objetivo de este trabajo fue construir un sensor de película fina con SnO_2 puro nanocristalino para obtener un dispositivo para detectar ppm de hidrógeno en aire y optimizar su comportamiento. Se eligió construir el sensor de H_2 para poner a punto las técnicas de película fina multicapas que luego se usarán en la construcción de un sensor fabricado con SnO_2 dopado con Cu_2O para medir ppm de SH_2 (g) en aire. El SnO_2 nanocristalino puro para medir H_2 fue sintetizado por tres técnicas de película fina cuyos resultados se compararon y caracterizaron por DRX, determinando el tamaño de cristalita (ecuación de Scherrer) y estudiando las tensiones generadas por cada film. Las películas delgadas debido a su espesor, a su depósito en capas múltiples y a los tratamientos térmicos a los cuales son sometidas, producen tensiones las que, a su vez, causan defectos tales como dislocaciones, bordes de grano, interfaces o intercaras, aglomeraciones de vacancias, etc. que aceleran los procesos difusionales de los gases en los materiales sensibles y, en consecuencia, mejoran la performance del sensor. También se caracterizaron los films por la técnica de absorción BET y se observó la morfología por HRTEM. Estas dos últimas técnicas se efectuaron en los primeros crecimientos. Técnicas de. SEM se emplearon para medir espesores de los films y la rugosidad o relieve de las superficies. Se realizaron las mediciones de la sensibilidad del sensor de H_2 y se compararon con datos dereferencia propia de los autores. Se describe también el circuito electrónico de control del sensor (de doble meandro obtenido por MEMS) que se ha mejorado mediante un nuevo circuito de medición microcontrolado, modular y transportable, que permite programar la temperatura de trabajo, los modos de operación del sensado, la calefacción y los tiempos de conmutación entre ellos.

Abstract

The semiconductor metallic oxides, like pure or doped SnO_2, have been intensively used for resistive thick film gas sensors to detect toxic, fuel or explosive gases: NO_x, SO_2, CO, H_2, CH_4 or VOCs (Volatile Organic Compounds) using thick film techniques. For many years, SnO_2, gas sensors (as based on microcrystalline materials) have been considered by its high sensitivity and relatively low operation temperature T_{op}=350^{o}C-450^{o}C for many years. If conventional microcrystalline SnO_2 is substituted by nanocrystalline SnO_2 to build the sensors, the authors have proved that sensor sensitivity increases from 30% to 35% and that the T_{op} decreases from (350-450)ºC to a range (180-220)ºC. In the last decade, nanocrystalline powders with high [surface/volume] ratio have been synthesized and applied reaching a considerable improvement of devices. As sensors work in oxygen atmosphere, the sensing mechanisms have been carefully studied for micro- and nanocrystalline SnO_2. In this case, a H_2 (g) sensor built with pure SnO_2 was chosen to carry out the multi-layered thin film techniques which will be used in a future experience to build a doped with Cu_2O - SnO_2 sensor to measure SH_2 (g) ppm in air. At first, H_2 (g) sensors were built at DEINSO with thick films. Techniques to build the layered nanocrystalline pure SnO_2 thin films were performed and they are going to be optimized. The nanocrystalline pure SnO_2 has been synthesized by three thin film techniques to compare results. Nanomateriales were characterized by DRX: crystallite size was measured by Scherrer equation and lattice stresses as produced by the different synthesis methods were also studied by X-rays diffraction. The thin films due to their thickness, to their deposit in multiple layers and to the thermal treatments to which they are subjected, produce stresses causing defects, such as: dislocations, grain boundaries, interfaces, vacancies clusters, etc. These defects accelerate the gases diffusional processes in the sensor, improving, in consequence, the device performance. Adsorption BET techniques and HRTEM morphology studies were performed on films. SEM was used to measure the films thickness and the surface relief or rugosity.

The double meander electronic circuit (built by MEMS) to control sensors (already patented by the authors) was also improved by a new controlled, modular and portable circuit, being able to program the working temperature, the sensing operation modes, the heating and the commutation time between them.

Palabras clave: *sensores de gases; nanopelículas cerámicas; nano-óxidos metálicos semiconductores; nano-*SnO_2*; sistema electrónico para control de sensores.*
Keywords: *Gas sensors; ceramic nanofilms; nano-metallic-oxides-semiconductors; nano-*SnO_2*;*
electronic system to control gas sensors.

1. Introduction

Semiconductive oxides (pure or doped SnO_2 among them) have been used to build resistive type gas sensors. As the oxide particles decrease to the nanometric scale, considerable changes are found in sensors built with nanomaterials. An increase of sensors sensitivity (30-37%) was observed in devices built with nanocrystalline materials in comparison with the sensitivity of sensors built with the same material but microcrystalline. With regards to the sensor operation temperature (T_{op}): the usual temperature range for conventional microcrystalline sensors (350-450)ºC decreases to a range (180-200)ºC for nanocrystalline sensors [1]. At first, the polycrystalline semiconductor was deposited on one face of an AlSiMg substrate; on the other face a heating circuit was built to reach the necessary high T_{op}. In case of sensors built with nanocrystalline materials [1], at first, semiconductive pastes were deposited as thick films. Pastes were prepared with SnO_2 powders, inorganic and organic additives [1-2]. Afterwards, pure or doped SnO_2, as prepared by dip-coating or spin-coating techniques with a previous sol-gel treatment or grown by spray-pyrolysis [3] were deposited. To be applied to this type of sensors, an electronic system with a microheater was designed and built by MEMS which operation is based in a circuit working with a commutation logic. The circuit, already patented by the authors [4], enables to measure the film surface resistivity (which results proportional to the concentration of the measured analyte) and, alternatively, to control the T_{op}. In this work, thin film sensors were built as layered system (three layers) deposited on a glass substrate to improve the device mechanical properties. The double meander electronic circuit built by MEMS [4] has been improved with a new modular and portable controlling microcircuit, being possible to program the operation temperature, the operation sensing modes, the heating and the commutation times between them.

2. Materials and Methods

1. *Nanocrystalline* SnO_2 *synthesis*

Three synthesis techniques have been comparatively used to grow the thin films:

--*Spin coating*: in this method a previous sol-gel synthesis is required with a precursor solution containing the cation from which the nanometric oxide thin film is desirable to be obtained. A solution of $SnCl_2.2H_2O$ in absolute ethanol is maintained in the ebb of a thermostatic bath at (80-85)ºC, forming at first the sol and later the gel. The sol is formed by an alkoxide which, after condensation, produces the gel, appearing long chains which increase the solution viscosity. The gel is used to produce the thin film by the deposition of few drops on a substrate and the system is undergone to a 3000 rpm rotation rate for 20s. To reach a measurable resistivity value, a minimal film thickness is required as obtained by the deposit of several overlapped layers, a preheating between each layer is undergone trying to avoid that, during the drying process, a layer could drag the previous one. Finally, an oxidation by calcination is performed at high temperature for a short time till forming the nanocrystalline ceramic material.

-- *Dip Coating***:** in this method the described sol-gel solution is also used. The film is prepared by immersing the substrate (hold by an extreme) inside a solution and taking it back in normal direction at controlled rate and temperature. These two last parameters determine the film thickness and microstructure. Previously, it was necessary to build at DEINSO the small equipment to deposit the films by the Spin- and Dip-coating techniques.

-- *Spray Pyrolysis*: an aerosol is produced with a solution of the cation salt ($SnCl_2.2H_2O$) from which it is desirable to prepare the thin film on the substrate projecting the aerosol on the hot substrate. Controlling the mouthpiece diameter, the distance and projection time, the thickness of the thin film will also be controlled. The Sn^{2+} to Sn^{4+} oxidation is produced by the contact of the hot surface with the atmospheric oxygen.

The materials characterization was performed with:

-- XRD diffraction to measure the crystallites size using the Scherrer equation [5] and to determine the stresses as generated by the different synthesis methods to prepare the nanofilms. Both studies were performed with Pananalytical Diffractometer, Empyrean Model with PIXCEL3D Detector from the XRD Laboratory, Department of Condensed Matter Physics-CAC-CNEA.

-- BET (Brunauer-Emmer-Teller isotherms) for adsorption measurements with an Autosorb-1 Quantachron Equipment, were only performed on the first grown films due to later equipment troubles. BET adsorption technique constitutes a basic form of surface analysis, highly relevant for nanomaterials and able to determine the specific area as expressed in [m^2g^{-1}]. This is usually performed by measurement of the volume of gas adsorbed onto a specific mass of sample, as a function of gas pressure being this measurement known as an adsorption isotherm. This technique will be again applied in the final characterization program.

-- Microstructure studies of films surface (surface relief or rugosity and thickness measurements were performed with a SEM-Philip 505, DEINSO-CITEDEF and the observation of he bulk pure SnO_2 films observations with a HRTEM, JEM-2100 (Jeol, Tokyo, Japan) were performed at the Josef Stefan Institute, Ljubljana, Slovenia.

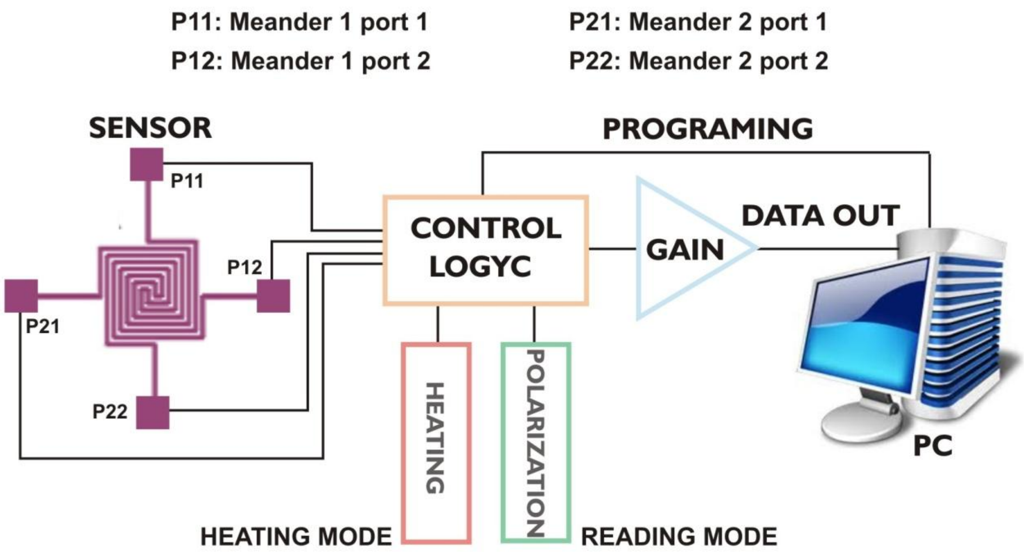


Figure 1: *Control electronics associated to the sensor. The detail of the double meander structure with four contacts is observe on the left.*

2. Heating platform and associated electronics

Previously, it was used the patented system [4] which enabled to alternatively measure the resistivity variation of sensor (proportional to the adsorbed gas concentration) and to control the device T_{op} to spare energy. To explain the use of the double Pt meander as heater and as electrodes for the signal extraction, it was taken into account to the ad-hoc electronics as described in the above mentioned patent, Figure 1.

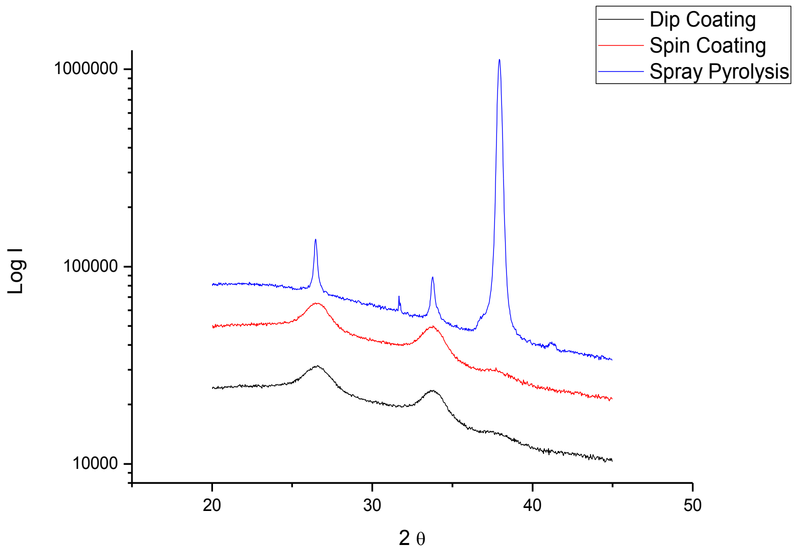
At first the sensitive material was deposited on glass substrates an afterwards on the Si_xN_y membrane, which is coating the Si wafer substrate) [3, 4]. The substrate is chemically etched in the central zone till reaching the membrane which mechanically supports the sensor structure. The system when functioning for a long time can damage the Si_xN_y membrane [3]. The structure minimises the thermal lost being possible to heat the sensor with a reduced power. This circuit was adapted since the thin films of nanocrystalline pure SnO_2 reach the higher sensitivity at an operation temperature range; Top = 120-150ºC. In this work, the designed electronic system was improved and a new controlled, modular and portable measurement microcircuit was built, which enables to program the operation temperature, the sensing response and the heating and commutation times between them.

3. Results and Discussion

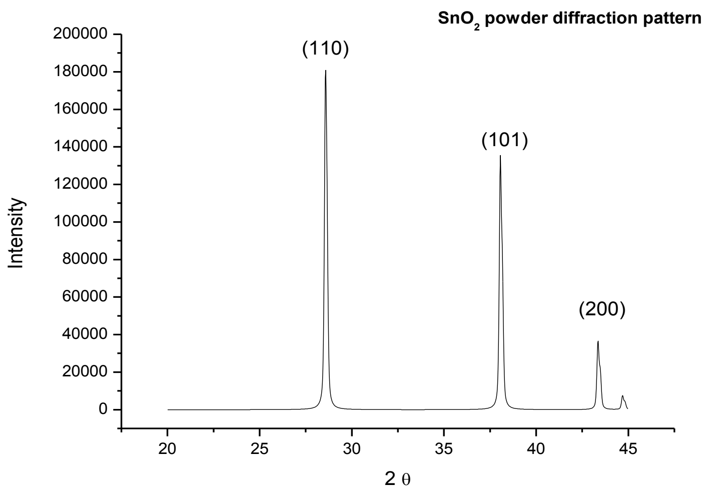
1. *Material characterization results*: The crystallite size depends upon the nanoparticles synthesis method and it is evaluated by XRD (Scherrer equation) [5]. Nanoparticles, as obtained by spin-coating or by dip coating exhibit smaller crystallites diameter [mean values: (8±1)nm-(9±1)nm, respectively] in comparison with the mean crystallites size for synthesis by Spray Pyrolysis reaching a mean value (150±6) nm.

XRD is also used to determine the lattice stresses of films as produced by the different synthesis methods [6]. Results of diffraction patterns of films prepared by spin-coating, dip-coating or spray pyrolysis are compared with the standard data of pure SnO_2 powder diffraction pattern [7] Figures 2a and 2b. It is observed in the spectra of the grown by the three techniques nanomaterials that the peaks shift towards smaller angles (ϴ), particularly, in case of the nanomaterials grown by layers techniques (spin-coating and dip-coating). The peak shifting towards smaller angles is due to the presence of stresses which are normal to the diffraction planes. This fact causes the expansion of the strained interatomic distance in comparison with the non-strained distance. According to Bragg law, the diffraction peaks will be shifted towards smaller angles. Other authors point out that some thin films appear to be in a complex stress state after their preparation [8, 9] even before being thermally treated. The small thickness of thin films produces (mainly by thermal action) important stress gradients acting as driving forces for diffusion. Mass transport in thin films is produced by grain boundaries and the high grain boundaries density in thin films contributes to increase the stress effects on the whole diffusion flux. Actually, the effect of stresses on diffusion and, consequently, on the sensors behaviour, are studied at DEINSO-CITEDEF.

BET adsorption measurements by BET - Brunnauer-Emmer-Teller isotherms enable to determine the specific area as before described [3]. Nano-SnO_2 microstructure was studied on the material surface by SEM and in the bulk by High Resolution Transmission Electron Microscopy-HRTEM [3]. Figure 3 shows a pure SnO_2- thin film HRTEM micrograph and its corresponding electron diffraction pattern as obtained with a JEM-2100 (Jeol, Tokyo) microscope, Josef Stefan Institute, Ljubljana, Slovenia.



2a)



2b)

Figures 2a and 2b*:* ***2a)*** *Diffraction patterns corresponding to specimen as synthesized by Dip-Coating (DC), Spin-Coating (SC) and Spray-Pyrolysis (SP) with a considerable widening of peaks for DC and SC specimen due to their smaller crystallite size. The mean crystallite size was calculated by Scherrer equation: (8±1)nm for SC, (9±1)nm for DC and (156±6)nm for SP specimens.* ***2b)*** *corresponds to the reference [7] standard diffraction pattern.*

Measurements of the resistivity variation in the H_2 (g) sensor have shown that the device results sensitive for ~ 20 ppm of gas in air at a Tòp ˷ 150ºC1. Otherwise, sensitivity depends upon the thin film thickness operation temperature (Top). These first results were compared with those of the thick film H_2 sensors built at DEINSO [1] showing that sensitivity was improved and that measurements could be performed at a lower Top.

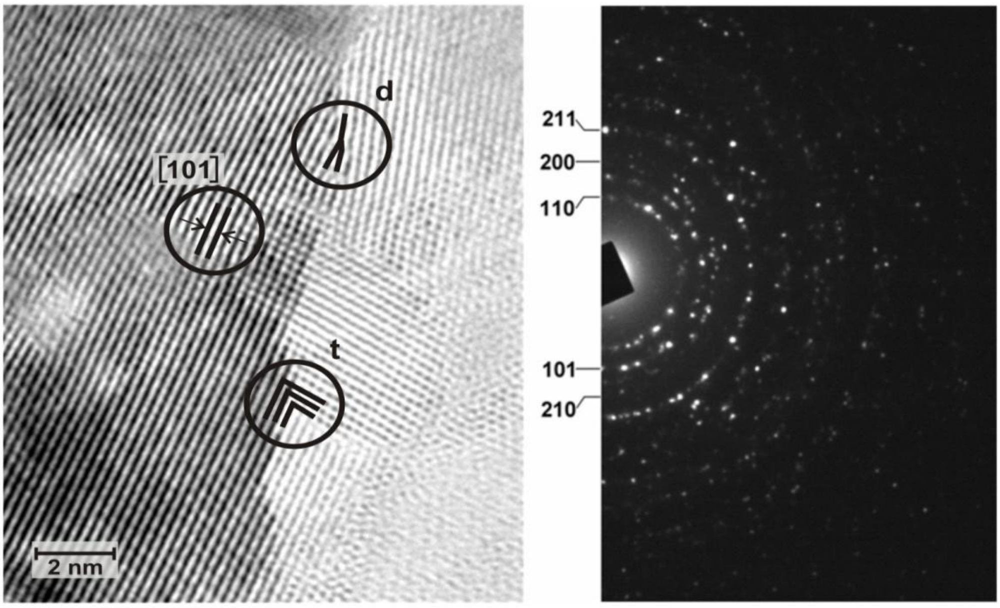


Figure 3: *HRTEM micrograph of the nanocrystalline pure SnO_2 film and the electron diffraction pattern. In the micrograph of* ***Figure 3*** *defects of the original film are observed like grain boundaries (crossing from up to down, dislocations (in the circle upper circle, marked as d), twined arrangement,in the circle marked t.*

2. Microheater temperature characterisation by power commuted excitation: Measurements were performed according to the scheme of Figure 4 to characterise the thermal behaviour of the system composed by the two heaters. One of them is heated and the response of the other resistor which, in this case, operates as temperature sensor (Pt thermal-resistor) is measured.

This fact enables to evaluate the response time of the heater-substrate, particularly its thermal inertia. The measurement set-up enables to excite with pulsated power one of the heaters and to measure with the other the temperature operating in thermo-resistor mode. This fact enables to evaluate how long the system remains heated after the elimination of the heater-power, resulting this evaluation essential to define the commutation times which are useful to stablish the strategy of the power administration for the MEMS type sensor.

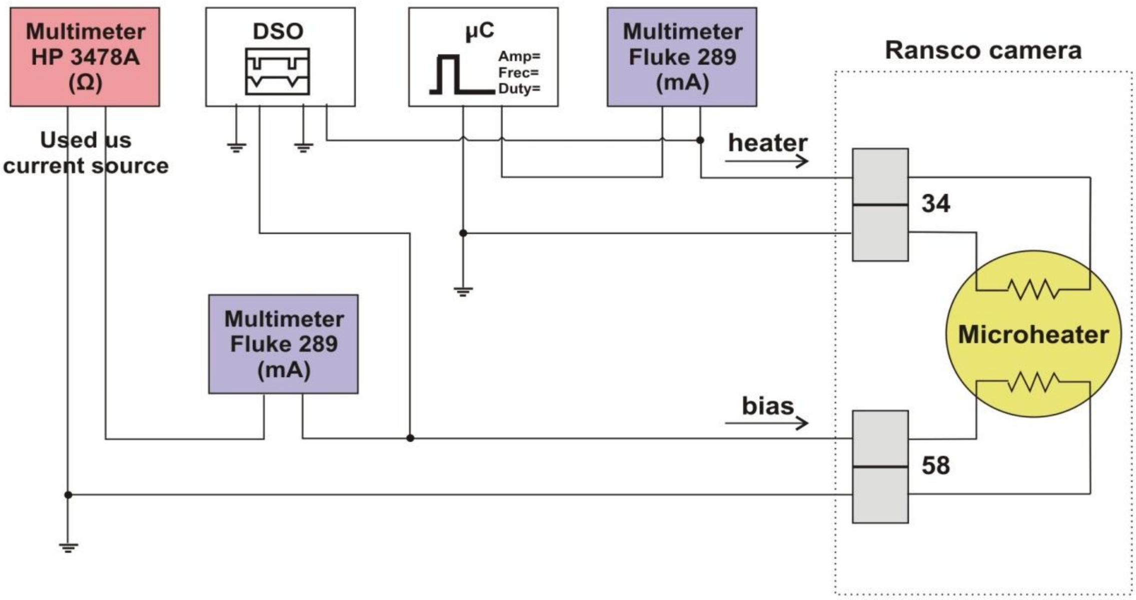
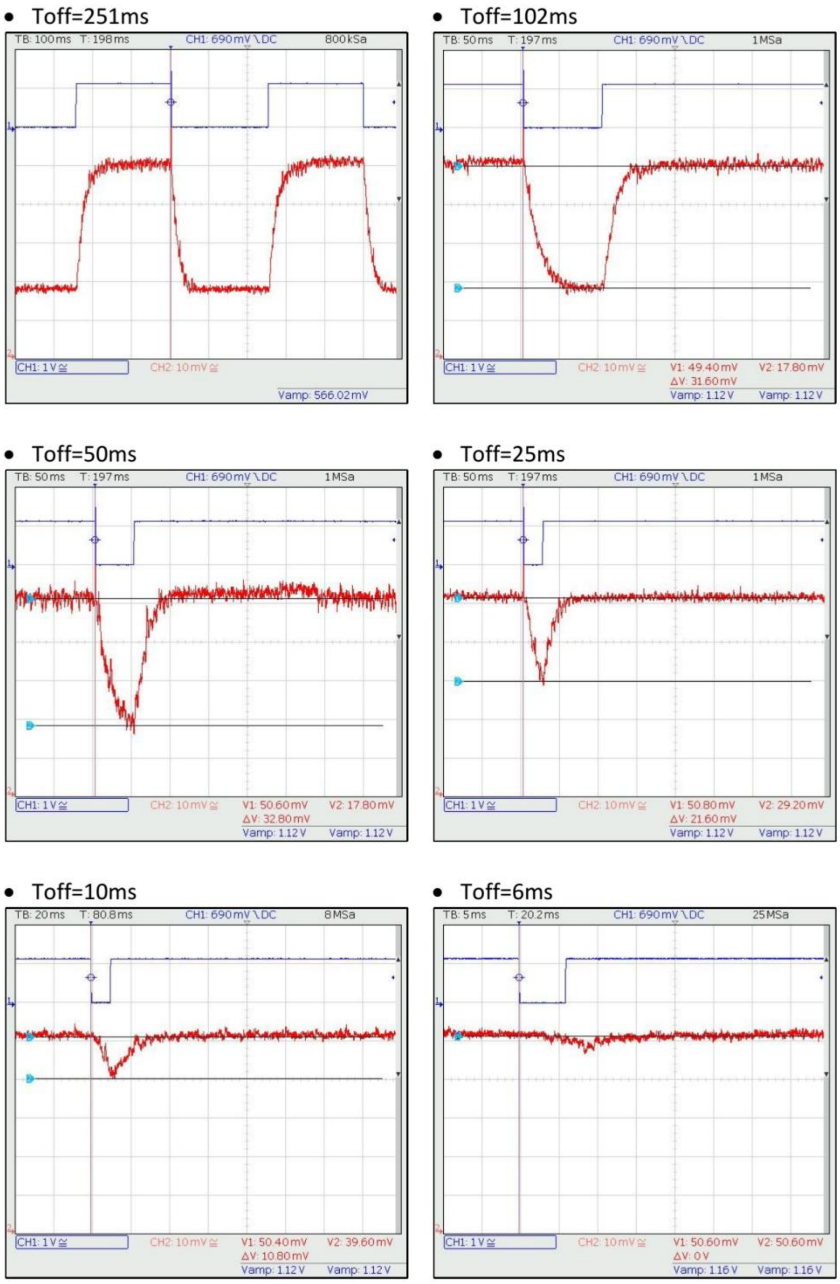


Figure 4. *Measurement circuit for the thermal response of sensor system*

As the polarization current of the heater (used as temperature sensor: meander 58 in Figure 4) is fixed, the current on this component will be modified proportionally to its resistance variation and, consequently, it will enable to measure the temperature variation. With this strategy, it is possible to prove how long it can be used without applying heating power and without reaching a significant temperature variation. The current on the meander, used as temperature sensor, is amplified to improve the signal visualization.

The measurement method was programmed to a microcontroller (Figure 5) in order to: 1) generate a square wave with period and pulse width regulated through two connected potentiometers, 2) filter the noise at the entrance of the analogic-digital conversors and 3) inform to the users by console the values of the configured parameters. Different work cycles are programmed till observing that the microheater (used as sensor) response would be approximately constant. The polarization current enables that the output signal could be different from noise being easy to be read in the oscilloscope scales, without reaching a value able to induce self-heating. According to that, in this case, a polarization current about 1mA was used (Figures 4 and 5).



Figures 5: *the generator pulse with which is excited one of the heating meanders is observed in blue and the substrate thermal response (as measured in the second heating meander) is observed in red, both considered for different times (ms)***.**

4. Conclusions

In this work, a thin film resistive H_2 (g) sensor was built with pure (catalysed with Ag) SnO_2 finding better results in comparison with those of thick film H2 (g) sensors [1] also built at DEINSO-CITEDEF. In fact, the sensitivity of the thin film sensor resulted: 20ppm in air in a Top range of (120-150ºC) and in case of resistive thick film H2 (g) in is 50 ppm and the Top range is: (180-200)ºC Spin-coating and Dip-coating are the chosen techniques to deposit the pure SnO_2 thin films to build the resistive sensors since both techniques generate larger stresses (as measured with XRD) than those produced by Spray.Pyrolisis. Defects like grain boundaries, dislocations, interfaces or vacancies clusters as generated by stresses are able to accelerate the gas diffusion in the sensors. Relations between stresses and diffusion are actually studied at DEINSO. With regards to the control of sensor performance, the electronic circuits developed at DEINSO have to be modified enabling the reliably measure and control of the sensor operation temperature to determine the heating/sensing cycles as well as to find the more convenient times to measure the sensing signal.

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