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Microstructural study of nanocrystalline pure and doped tin dioxide to be used for resistive gas sensors

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ABSTRACT

Nanocrystalline pure and doped SnO_2 have been intensively studied for a long time to build resistive gas sensors. However, it is still useful to synthesize nanopowders with the smallest crystallite size to build devices. A modified gel-combustion method and a novel reactive oxidation process are proposed for nanopowders synthesis and results are compared. Materials have been characterized by XRD, Scherrer equation to evaluate the crystallite size; BET absorption to determine specific area and HRTEM to observe the crystallites (evaluating their mean size and distribution); defects and effect of calcination treatments are also considered. Previous studies have shown that if nano-SnO_2 replaces the conventional microcrystalline-SnO_2 to build resistive gas sensors, sensitivity increases (>30%) and the operation temperature considerably decreases.

A heating and measuring system has been designed for achieving low power consumption and uses pulsed heating operation. This method of electrical control and measurement is operated intermittently, with "heating" and "readout" cycles (readout: signal of sensitive film).

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1. Introduction

Tin dioxide semiconductor (SC) has been used to build gas sensors for many years, exhibiting interesting properties which considerably change as the SnO_2 grain size decreases to nanometric dimension. Pure and doped nano semiconductors were studied and already applied for resistive gas sensors [1–7]. The replacement of the conventional microcrystalline pure or doped SnO_2 by the same material but nanocrystalline to build the gas sensors, has driven to interesting results since the sensor sensitivity increased (30–37%) and the operation temperature (T_{op}) considerably decreased from 350–450 °C to a range: 250–350 °C for nanocrystalline Al-doped SnO_2, and similarly for In doped SnO_2. Fig. 1 or to 180–220 °C for pure nano-SnO_2 [8–10], Fig. 2. The gas detection process is affected by several factors, among them the microstructure. The metallic oxide previously reacts with the air oxygen forming at the SC-surface oxygen adsorbates, (O^-, O_2^-, O^{2-}) [11–13] which play an important role in gas sensing (being the O^- the most active). The adsorbates cover the SC-surface and the grain boundaries and react at the $T_{op} \sim 350$–450 °C if the sensor is built with microcrystalline semiconductor. In case of *n*-type SC metallic oxides, the formation of these adsorbates builds a space–charge region, resulting in an electron-depleted surface layer (space–charge) due to the electron transfer to the adsorbate as follows:

$$O_2(g) + 2e^- = 2O^-(\text{adsorb.}) \quad (1)$$

The depth of the space–charge is a function of the surface coverage with the oxygen adsorbates and of the intrinsic electron concentration in the bulk. The resistance of the *n*-type SC is, in consequence, high because a potential barrier to the electronic conduction is formed at each grain boundary [11]. If the sensor is exposed to a reducing gas (i.e. CO) at the T_{op}, the gas reacts with oxygen adsorbate (O^-) according to:

$$CO + O^- = CO_2 + e^- \quad (2)$$

The oxygen adsorbates are consumed by the subsequent reactions, so that a lower steady-state is established, the potential barrier height decreases and a resistance drop is produced, being the resistance variation the measuring parameter of sensor. A simple schematic model for grain-size affecting the surface resistivity was proposed by Yamazoe et al. [11] concluding that the sensor sensitivity increases as grain size decreases. The sensor sensitivity (S) can be defined as: $S = R_{air}/(R_{air+gas})$, where: R_{air} is the resistance in air and R_{gas} is the resistance in a gas sample containing a reducing

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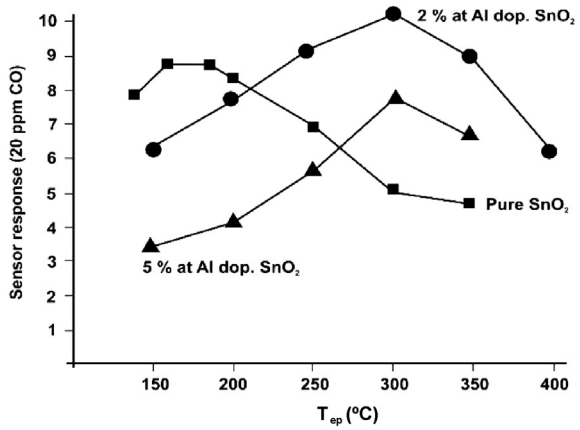

Fig. 1. Sensor response to 20 ppm CO (g) for doped SnO_2 (at%) vs. T_{op} (°C).

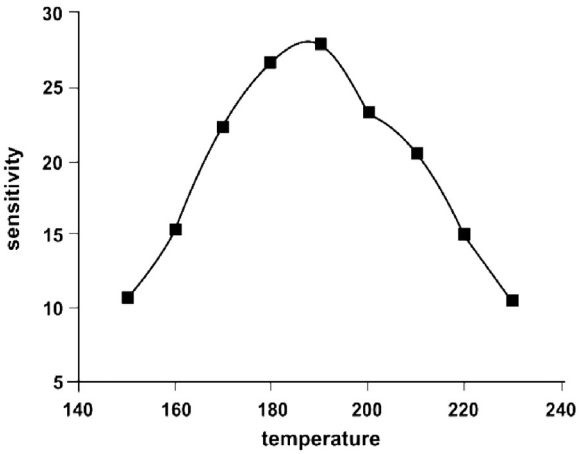

Fig. 2. Sensor sensitivity to 5 ppm H_2 for pure SnO_2 vs. T_{op} (°C).

component. The reactivity of the oxygen adsorbates is a function of the type of reducing gas and of sensor temperature.

The aim of this work was to analyze the structure and morphology of pure and doped (with Al or In) nanocrystalline SnO_2 with different crystallite diameters (Ø), to be applied for gas sensors. Nanomaterials were prepared by gel-combustion [14] and/or by reactive oxidation with H_2O_2 [15] and results of both methods were compared with similar results [7]. Characterization was performed by X-ray diffraction (XRD), Brunauer–Emmer–Teller isotherms (BET) method and High Resolution Transmission Electron Microscopy (HRTEM).

2. Experimental

2.1. Pure SnO_2 synthesis

Pure SnO_2 nanopowders were synthesized by two techniques and results are compared as described in [7]: reactive oxidation with H_2O_2 [15] and modified nitrate–citrate gel combustion [14]. In the first method, the $SnCl_2$ reacts with H_2O_2 treating afterwards the product with $(NH_4)OH$ in H_2O_2 medium. Stannic acid is produced giving nanopowdered SnO_2 by calcination:

$$SnCl_2 + H_2O_2 \rightarrow SnOCl_2 + H_2O$$

$$SnOCl_2 + 2(NH_4)OH \xrightarrow{H_2O_2} SnO_3H_2 + 2(NH_4)Cl \xrightarrow{\text{calcination}} SnO_2$$

The violent oxidation reaction with H_2O_2 disintegrates the product particles yielding small crystallites with diameters: 2–9 nm.

The *gel-combustion*, fuel-rich synthesis [14] starts with the preparation of a precursor: (aqueous solution with p/a metallic Sn), 70% – HNO_3, CH_3COOH and 25% – NH_4·OH. Citric acid is the organic fuel; [tin/fuel] ratio = 1:6. The pH was increased with (NH4)OH (approaching to neutrality and keeping the solution homogeneity). The solution is thermally evaporated till turning into a gel. If heating is sustained, gel turns into a darken foam which ignites. The intense combustion of the final stage is due to a highly exothermic redox reaction between the oxidizing nitrate ions and the organic fuel. TGA plots of gellified samples show that gels usually liquefy at ~80 °C and ignition starts at ~200–300 °C. Combustion usually promotes an ignition not depending on atmospheric oxygen supply, since the foam bubbles are filled either with NH_4NO_3 vapours or NO_x ($1 \leq x \leq 2$) restricting the oxygen access to the bottom of reaction container. Combustion duration is short: usually, half of a minute. Gas liberation promotes the fast disintegration of precursor gel at high temperature causing decomposition. If the oxide contains carbonaceous residues by a fuel surplus, they are removed by calcination and nanometric crystallites (9–15 nm) are produced. Parameters to be fitted are: organic fuel type, combustion temperature and process duration. After the synthesis, the crystallites size and homogeneity, their morphology and the impurities retention during the synthesis process have been evaluated.

2.2. Doped SnO_2 synthesis

The gas sensor to detect hydrogen was built with nanocrystalline pure SnO_2 [9] CO (g) ppm was built with Al-doped nanocrystalline SnO_2 [8] and that for VOCs sensing [10]. The method to prepare the two first materials was gel-combustion using CH_3COOH as fuel and the crystallite size resulted: 2–4 nm. In case of In-doped nanocrystalline SnO_2 [10] the synthesis method consisted in precipitating together p/a $SnCl_2{\cdot}2H_2O$ and $InCl_3$, in NH_4NO_3 medium to produce stannic oxo-hydroxide which was intensively oxidized with 30–250 vol H_2O_2 thus obtaining stannic acid as nanocrystalline powder. This solution was precipitated with $(NH_4)OH$ to get an homogeneous compound of stannic acid and indium hydroxide. The resulting crystallite size was ~2–4 nm.

2.3. Characterization of nanomaterials

XRD enabled to identify the material, to evaluate the crystalline structure and to measure crystallites size by application of Scherrer equation; BET measurements were used to determine the specific area and HRTEM, Fig. 3a and b, enabled to observe the crystallites morphology, size and distribution and the calcination temperature effects.

2.4. Sensors building and heating/measuring system

This item is a brief description of functional principle of the sensor gas by direct contact.

In case of using pure or doped nano-SnO_2 to build the sensor and to reduce the power consumption, an innovative heater and measurement device [16], similar to those used for thin film sensors [17], was developed with MEMS Technology (Closed Membrane Type).

The sensor can work in pulsed mode, just as other sensors do, similar to those of the international market. But, differing with them, the sensor described in this work exhibit direct thermal and electrical contact with the sensitive film. This fact enables to reduce a step in the manufacturing process because it is not necessary to isolate the sensitive film and the heater (passivation layer and annealing are not required). This situation improves the efficiency

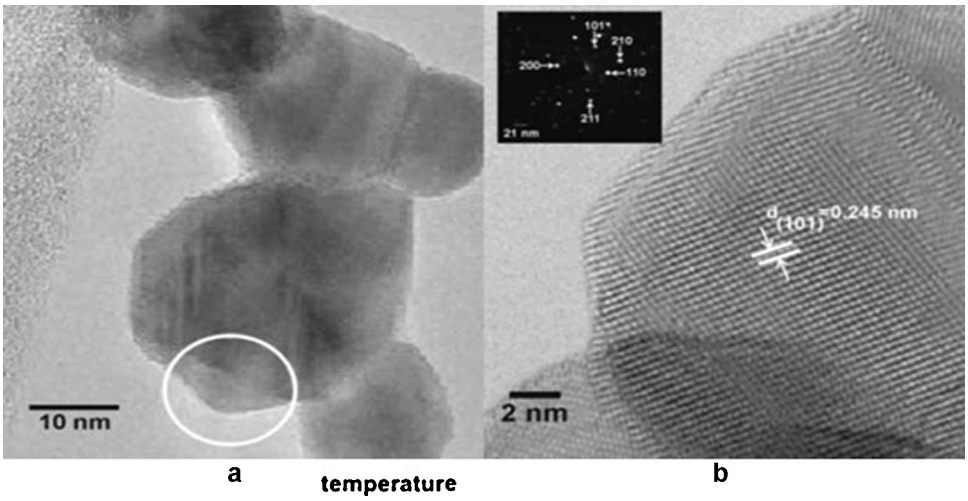

Fig. 3. (a) HRTEM micrograph of SnO_2 crystallites (calcination temperature: 700 °C) and (b) Detail of the crystallite shown in (a) (circle) at higher magnification. Defects are observed and twins, dislocations and grain boundaries are shown by arrows.

to transfer heat from the heater to the sensitive film and it also is possible to increase the contact area between the sensitive film and the read-out.

Different gas sensors of SC type, which functioning principle is based on the variation of sensitive film conductivity by interaction with a gas to be detected, requires control of the temperature by a micro-heating device.

The temperature on the platform can be programmed enabling to catalyze a surface chemical reaction, which is electrically measured by the conductivity variation of the sensitive film.

Read out signal, is measured with a trans-impedance amplifier circuit [18] and which is used to evaluate the gas concentration. The micro-heater operation temperature will be confined to the silicon nitride membrane in the active area to perform a periodic heat cleaning (400 °C on the sensing layer).

In Fig. 4, it is shown the temperature distribution on the double meander (100 mWatts heating power) by electro-thermal simulation.

The Fig. 5 shows the micro-heater architecture built on a silicon wafer ⟨1 0 0⟩(thickness 450 μm) with a low stress LPCVD Silicon Nitride layer (minor than 200 MPa) and thickness between 0.8 and 1 μm

In Fig. 6 it is shown the micro-heater packaged (gold heater and chromium interface layer). Pt was the chosen material for the

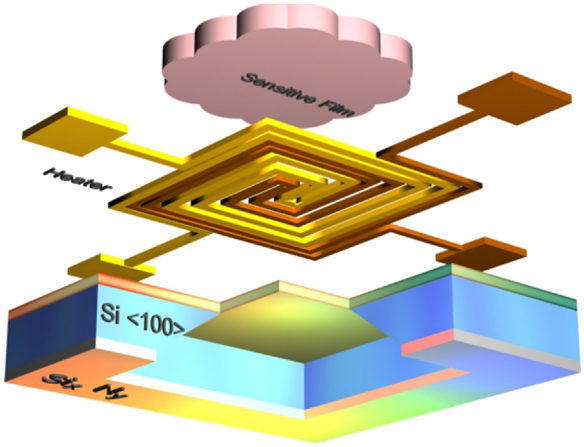

Fig. 5. Scheme of micro heater in the released silicon nitride membrane.

device with an adherent titanium oxide interface (coating) to avoid migration problems on the sensitive film.

The device was fabricated on a micro-machined silicon structure performed with the wet-etching technique (with KOH). The SixNy layer was used to stop the etching in the micromachining process and to function as a thermal isolation structure [19].

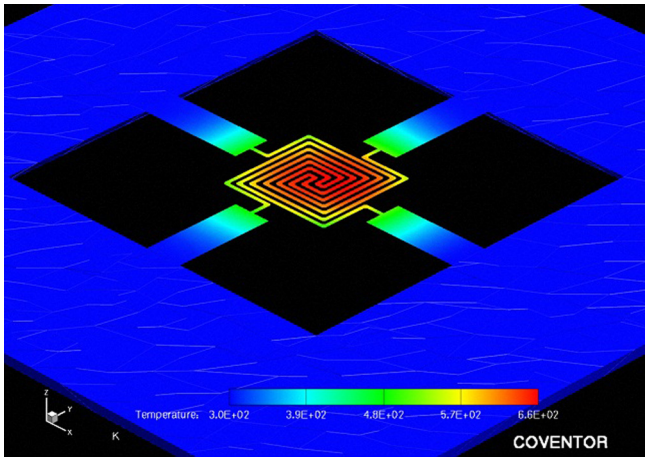

Fig. 4. Temperature distribution on the double meander (100 mWatts heating power) by electro-thermal simulation.

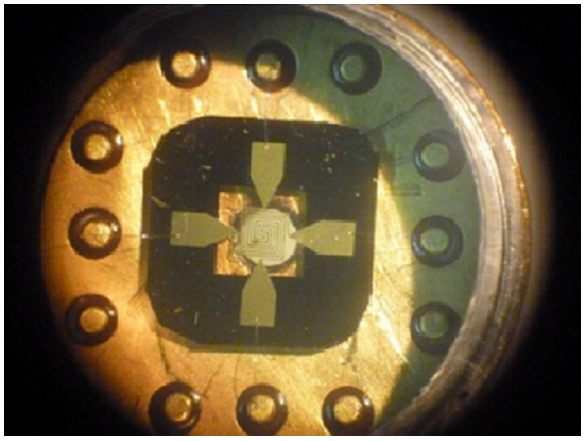

Fig. 6. Sensor on TO-8 package and wire bond details. The active area is surrounded by the transparent membrane which is supported by the outer silicon ⟨1 0 0⟩frame.

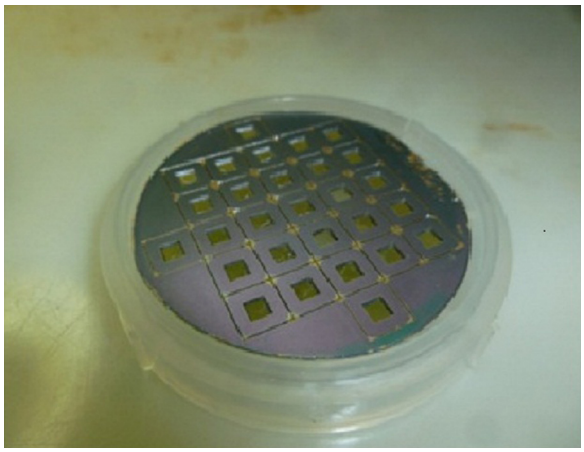

Fig. 7. Micro-machined (back side) of ⟨1 0 0⟩ silicon wafer with the closed released membrane.

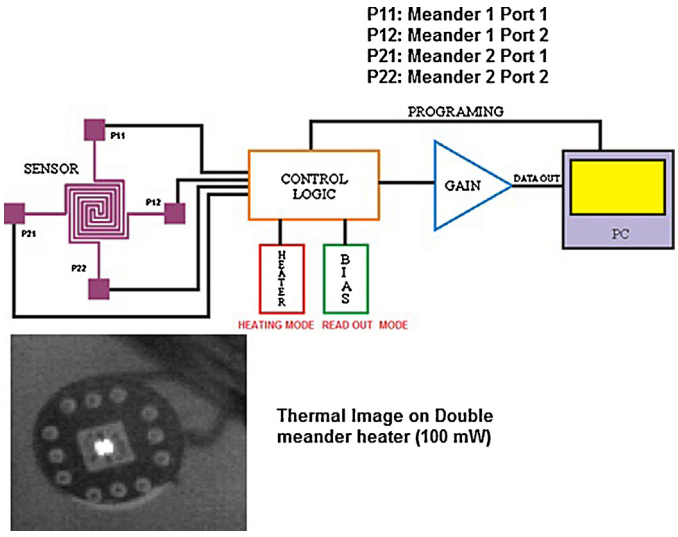

Fig. 9. Scheme of the sensor, electronic controlling switched mode (heating mode and read out mode) and thermal image of micro-heater.

Fig. 7 shows a ⟨1 0 0⟩ silicon wafer with the released membrane, which enables to define the area where the micro-heater is integrated. Due to the membrane low residual stress and small thickness (approximately 1 μm), it is possible to open square windows ($1.5 \times 1.5\,mm^2$) for the active area. A Au heater (preliminary test) with double meander structure is integrated to SixNy membrane forming the heater-contacts system, working in switched mode. The double meander structure is centred on the released membrane of substrate SixNy. This assembly is used to improve the device thermal isolation and to reduce the power consumption.

This structure is used to heat the sensitive film and to get the read out signal, enabling to improve the thermal and electrical contacts. The sensitive film is printed by standard screen printing technology and annealed before micromachining process.

The double meander structure is used both, as heater and electrical port for the sensitive film (read out mode). The double mender is related to the ad-hoc electronics shown in Fig. 8. A portable device can be built if the arrangement is provided with a microcontroller and it associated electronics (Fig. 9).

The Data Logger & Calculation block enables the storage in time of the measured conductivity values and their translation to the gas concentration.

The device operating logic is:

(I) The sensor electrodes are excited, for a period of about some milliseconds, by the heater block which delivers the necessary power for correct functioning (cleaning mode $T = 400\,^{\circ}C$ and pre heating for read out mode $T = 250\,^{\circ}C$). In this heating stage, the two meanders (resistors), are serial connected. Once removed the heating power, the sensor temperature is maintained during in a fraction of a millisecond (Fig. 10).

(II) After heating, the control-logic switches the double meander contacts to pick up (Read Out mode with a Interrogation pulse) and enables the bias block to excite the terminals to the adequate polarization levels on the sensitive film, during a few microseconds (Sensitive film temperature is approximately $250\,^{\circ}C$).

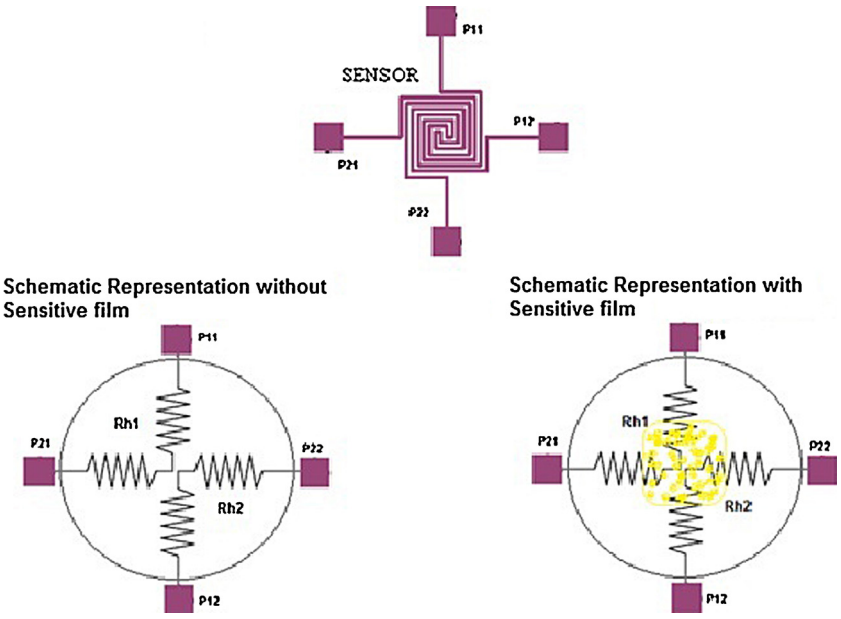

Fig. 8. Double meander detail and schematic representation.

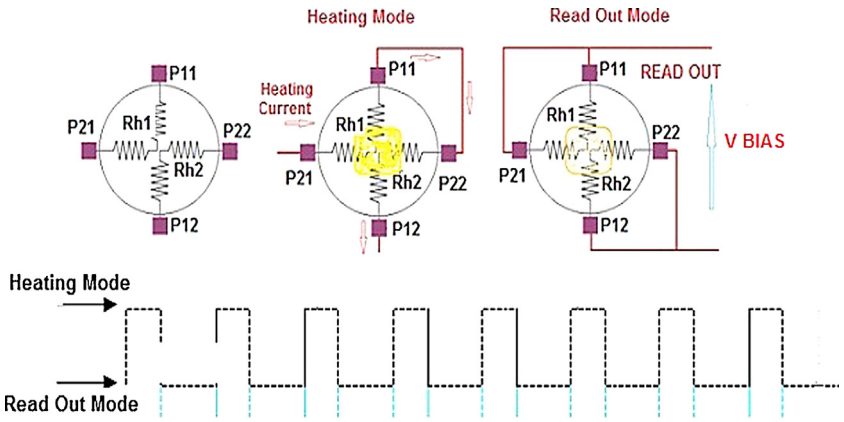

Fig. 10. Schematic representation details, of Heating and Read Outmodes.

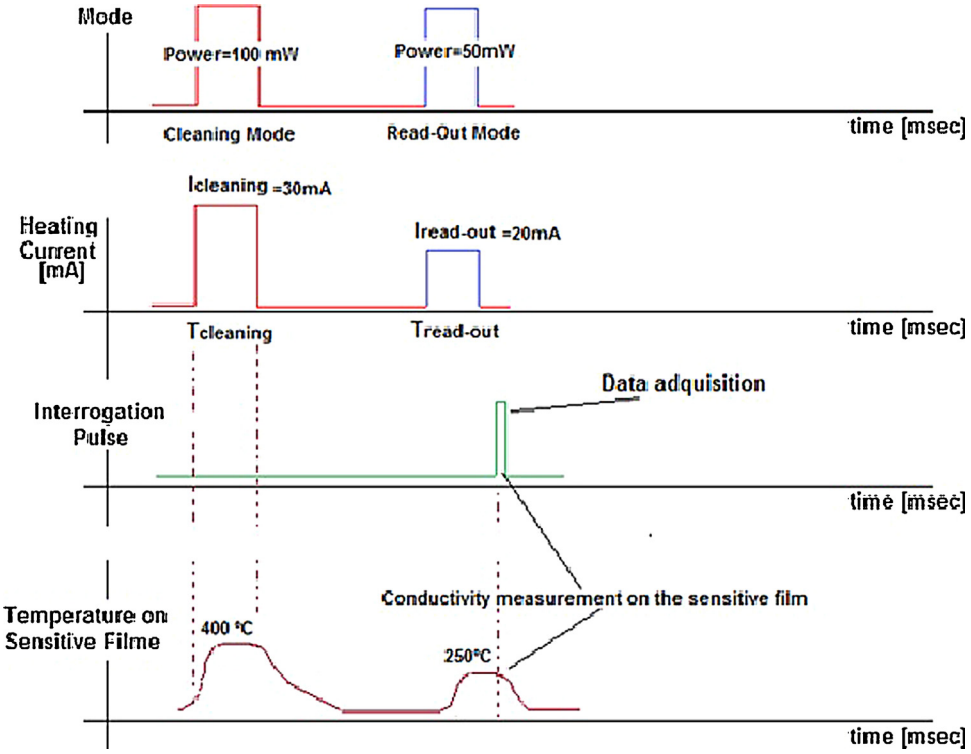

Fig. 11. Timing details to perform the logic operation of device.

(III) The acquired data are stored being repeated the whole process according the programming. Details of timing can be observed in Fig. 11.

3. Conclusions

Pure and Al and In-doped SnO_2 with different crystallite size ($\acute{O}$) were synthesized to build resistive gas sensors (to detect H_2, CO and VOCs) by a gel-combustion method [$\acute{O}$ = 9–15 nm] and by a reactive oxidation with H_2O_2 [$\acute{O}$ = 2–9 nm]. XRD, BET absorption technique and HRTEM were applied to characterize the structural and morphological properties of SnO_2. Calcination temperature causes the grain size growth contributing to decrease the specific area. The analysis of XRD spectra for different sized crystallites always enabled to identify the rutile tetragonal phase for doped SnO_2. HRTEM micrographs have shown that rounded nanoparticles with the smallest grain size were homogeneously distributed and exhibited higher defects density.

Calcination at higher temperatures caused crystallites with larger grain size exhibiting faceted form and considerably lower density of defects. Sensors built with nano-SnO_2 to detect H_2, showed a sensitivity value (~35%) higher in comparison with that of reference sensors, being the highest sensitivity value and the T_{op} decrease to ~180–200 °C related to the smallest crystallite size. In case of sensors built with pure or doped nano-SnO_2. Because of their lower T_{op}, a commutation: heater to measurement device was developed to be incorporated to the sensor.

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Cristian L. Arrieta graduated in Electronic Engineering at National Technological University (Facultad Regional Bs. As.) on 1999. From 1998 he is a researcher in CITEDEF (Institute for Scientific and Technological Research for the Defence). His present research area includes Micro-Electromechanical Systems, Optical Devices and Electronic Circuit engineering. From 1999 he is an Associated Professor and Lecturer at the National Technological University (UTN), he teaches Circuits Theory and Electromagnetics. He has published some scientific papers in international reviews, one invention patent and reports for the local industry.

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