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High accuracy measurements of new conductometric metal oxide gas sensors by efficient control of working conditions

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***Abstract*-**A measurement system designed for characterizing resistive metal oxide sensors based on novel materials is described. The system can simultaneously test up to 8 sensors. It exploits an ad hoc structure based on an alumina substrate equipped with electrodes, a heater and an accurate temperature sensor, on which the material under study can be easily deposited by screen printing, spin coating or dip coating. The system allows for studying the sensor behavior by accurately setting the operating conditions in terms of environment composition, gas flow, humidity and temperature. The system is fully programmable and it individually controls the chemical film temperatures and it measures these quantities with a resolution close to 0.1 °C. Experimental results show that the designed system can detect the targeted gases in real-time and accurately quantify their concentrations.

I. Introduction

Solid state gas sensors still attract the attention of many researchers, as there are the basis of the development of reliable on-line low-cost measuring equipment. These latter can be used in many different application fields, from air-quality and process control monitoring, to food quality assessment and homeland security.

Particular attention has been devoted to the development of conductometric gas sensors based on metal oxide (MOX) sensing materials, because their low-cost production process and their optimum sensitivity and stability make MOX sensors the ideal candidates for the development of low cost systems. Among different types of MOX, SnO_2 and ZnO have been thoroughly studied in the last four decades, and they are already used also in commercial devices, even if some problems related to their use are still open. For this reason, in the recent years, many research efforts have been devoted to the preparation and to the study of new metal oxides. To this purpose, in order to characterize novel MOX sensors and to derive their performance parameters, a reliable, versatile and high performance measurement system is needed. The sensing mechanism of MOX conductometric sensors is very complex: it depends on the solid-gas chemical reactions and on the physical phenomena related to electronic conduction. The chemical-physical behavior of the sensor is very difficult to be observed and often remains the subject of hypotheses: the material composition as well as of both bulk and surface structure, the crystal bulk and surface defect population and the sensor micro- and macro-structure are crucial aspects for the electronic conduction in the sensors, that are almost impossible to be a-priori predicted, [1]-[10].

It is also known that MOX sensors performance is heavily influenced by working conditions, such as temperature, humidity, and presence of interfering gases. For this reason the sensors characterization should be performed in experimental conditions that grant for a very accurate knowledge of the surface temperature and of gas flow composition, also in terms of humidity.

This paper describes a real-time electronic measurement system which can perform an overall characterization of 8 conductometric MOX gas sensors at the same time. The system was developed exploiting a real-time National data generation/acquisition system, and ad hoc developed front-end electronics. A PC, that controls the entire system, allows to set the measurement conditions (gas flow composition, sensor temperature, measurement protocol) and to perform data processing. These features make the system suitable for both determining the performance indexes of a gas sensing device (e.g., sensitivity, stability, selectivity, response/recovery times) as a function of various combinations of measurement conditions, and for validating sensor models in an adaptive way.

II. System Architecture

A. Sensor structure

A substrate for the facile development of conductometric gas sensors was developed (see the inset in figure 1), which allows the test of new materials prepared as micro or nano-structured powders. Two electrodes for the chemical resistor and a platinum based resistance temperature device (RTD) are spread out by screen printing on one side of a 0.25 mm thick alumina substrate; on the other side a heater resistor is deposited in the same way.

B. Measurement system overview

The system, as shown in figure 1, consists of three main blocks: the chemical sampling system, the conditioning and acquisition electronics and the host computer which manages the overall experiment and store data. The chemical sampling system consists of up to 9 digitally-controlled flow-meters (operating in the range from 5 mL/min to 500 mL/min) that are used to set the flows of the reference gases coming from gas tanks. One of these flow-meters is usually dedicated to the carrier gas (nitrogen or synthetic dry air) and the other ones to mixtures consisting of the carrier gas and target gases with known concentrations. The flows are mixed in order to obtain a selected concentrations of the target gases. The humidity level is set by a water bubbler, kept at a fixed and known temperature by a thermostatic bath, fed by the carrier gas.

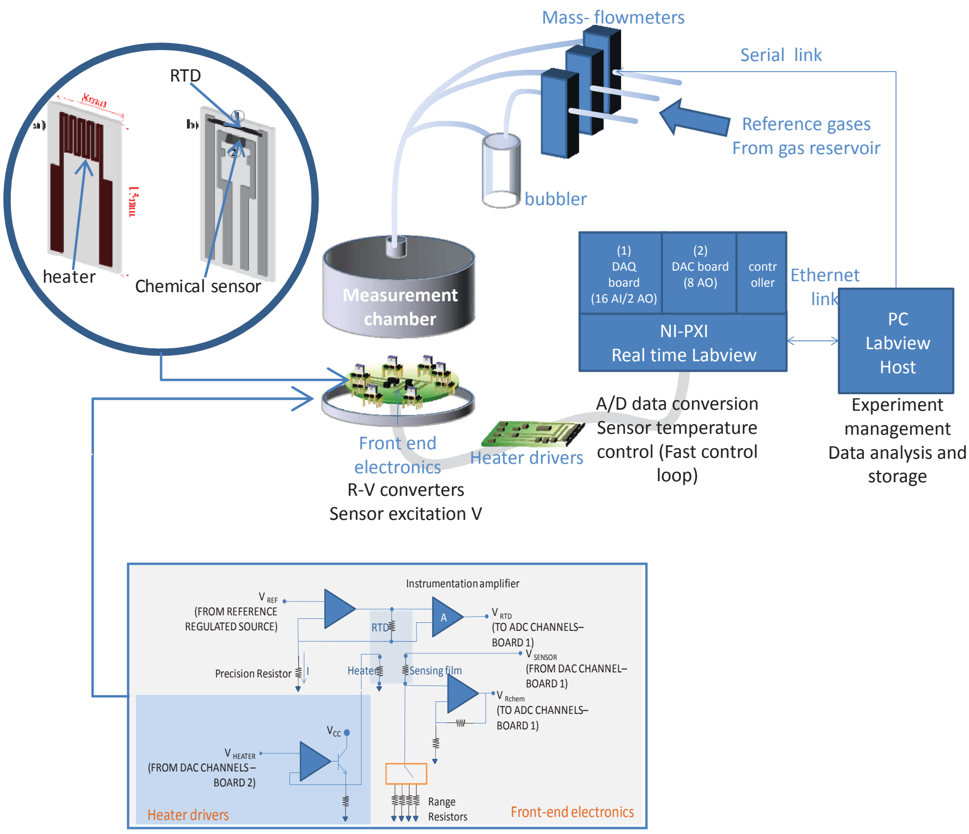

Figure 1. System overview

During the measurements the total flow is kept constant inside the chamber, whereas its composition can be varied, by changing the flow-meter set points. This allows to test the sensor under chemical transients or in different steady-state chemical conditions. An important part of the chemical sampling system is the chamber, which consists of a cylindrical stainless steel structure that can host up to 8 sensors mounted on a circular array. The symmetry of the chamber grants nominally equal chemical testing conditions for all the sensors.

The conditioning and acquisition electronics comprises: eight front-end boards, a board containing the heater drivers, a real time PXI system equipped with a 8 analog output board, a 16 single ended analog input board and a controller for real time operations.

Each front-end board hosts the conditioning electronics for the measurement signals. As it can be seen in figure 1, a R-V converter, based on a constant, accurate and stable current generator and on an instrumentation amplifier is used for the read-out of the Pt-RTD value. The chemical film resistance is converted into a voltage by a voltage divider with selectable high precision reference resistances.

The conditioning circuits, needed for heater driving, are placed on a different external board, connected via a flat cable to the front-end boards. The analog measurement signals are fed to sixteen 16-bit A/D converters on a commercial acquisition board (board 1, National Instrument PXIe-6361) hosted in the PXI system. The excitation signal for the heaters is generated by a DAC board with 8 analog outputs (board 2, National Instruments PXI-6713) in the same PXI crate. Finally, a controller board provides the management of acquired data: it executes a real time program with a 200 kHz timing, which performs sensor signal reading and a low level PID control loop for temperature control, that uses the temperature reading from the Pt-RTD to set the power dissipated by the sensor heater.

C. Film temperature measurement and control system

Using the Pt-based RTD screen printed sensor on the alumina substrate and the front-end electronics described in the previous section, the voltage output, VRTD (see figure 1), is linearly related to the film temperature. In particular (some symbols are defined in figure 1):

$$\Delta V_{RTD} = R_0 I A \alpha \Delta T_{RTD} \tag{1}$$

where α is the temperature coefficient of the RTD, R_0 its value at 0 °C, and T_{RTD} is the average RTD temperature.
The thermal system can be represented by this simplified linear lumped parameter model:

$$G_{TH} T + C_{TH} \frac{dT_{TH}}{dt} = P + G_{TH} T_{ENV} \tag{2}$$

where G_{TH} is the system thermal conductance (convection), C_{TH} the system thermal capacitance, T_{ENV} the environmental temperature, T the sensor average temperature, and P the power dissipated by the heater.
The control loop implements a simple PI controller as follows:

$$\begin{aligned} P_{k+1} &= P_k - \gamma t_c e_k + \beta(e_k - e_{k-1}) \\ V_{HEATER,k+1} &= \sqrt{P_{k+1} R_{HEATER}} \end{aligned} \tag{3}$$

where γ and β are the control loop parameters, t_c is the loop period while e_k represents the difference between the measured temperature and the desired one at k-th step and P_k the power dissipated by the heater, [3][4].
The described control algorithm and system allow to accurately set the working temperature of the sensing film: the resolution of the temperature measurement and setting is close to 0.1°C, but it requires an accurate sensing device able to grant a high temperature measurement accuracy. A reasonable requirement for the application is to obtain an overall accuracy close to 1°C. This requisite can be hardly met by realizing the RTD sensor by screen printing technology, which allows for a reproducibility of device in terms of R0 and α of some per cents.
In order to obtain highly accurate measurements of the temperature, one of the sensor slot was used to host a substrate, where the chemical sensor film is replaced by a commercial miniaturized PT-100 class A sensor (1.6mm x1.2mm). The temperature measured by that micro device (±0,63°C up to 240°C) can be used as a reference temperature in an automatic calibration procedure of the screen printed RTDs, which is used to enhance the RTD sensor accuracy up to the required limit.

D. System software and its programming capability

In general the complete functionality of the system is achieved by having two LabVIEW VIs: the first is executed on the host PC, and the second VI is deployed on the target PXI and executes a real time loop. The system is programmed to perform the following general tasks:

- Open Loop Operation. This task is performed with new sensor arrays before starting the measurements. It is used to calibrate the screen-printed RTD sensors. All sensor heaters are forced to dissipate the same power for a time sufficient to reach the steady state, then the RDT resistance and the reference temperature values are measured. This step is repeated for different power values (usually 10 values covering the operation temperature range). After that the system assesses by linear fitting the temperature coefficient α, and the R_0 value of the screen printed RTD. In this phase the temperature control loop parameters γ and β are evaluated too, given the desired rise time and a proper damping ratio. This stage is considered as a calibration phase and the calculated parameters will be used in the following phases. Environmental temperature and humidity inside the chamber are independently measured by two dedicated sensors.
- Closed loop operation. Two types of measurements can be performed. 1) Tests in transient chemical conditions at fixed temperatures that can be repeated at each temperature (in order to assess stability and repeatability). This allows to study the sensor response dependence on temperature and on gas concentration. 2) Tests in fixed chemical conditions, but variable temperature, which is useful for model validation [3]. The host VI downloads the parameter values obtained in the open loop characterization phase (α, R_0, γ and β) for each of the 8 sensors; then it downloads the measurement parameters, namely the temperature setting points or profiles, and starts the PXI real time module which performs the measurement-control loop with cycle time of 5 μs. While the measurement is going on, the host reads data from the PXI module, controls the settings of the flow-meters and displays and saves data.

III. Experimental results

Some experimental data are shown in figure 2. In figure 2a) the results, obtained while operating the system in open loop with four power steps (1.0W, 1.2W, 1.4W and 1.6W), are shown. Each sensor is driven by a V_{HEATER} specified by the desired power value once its resistance value is known; at the same time the temperature is measured through the reference commercial PT-100. At the end of the fourth step, an embedded fitting function is performed to calculate α, and R_0 for each sensor. In figure 2b) the temperatures, measured by the calibrated screen printed RTD, are shown when the system is operating in closed loop, controlling the temperature in order to follow a specific profile consisting of temperature steps. The obtained performance is satisfactory: for instance, the open loop thermal system has a time constant of about 10s whereas, when avoiding saturation of the heater voltage, the closed loop grants a rise time of about 1s. This ensures, in many conditions, a thermal transient faster than the chemical one, induced by temperature changes, and allows to apply transient temperature testing.

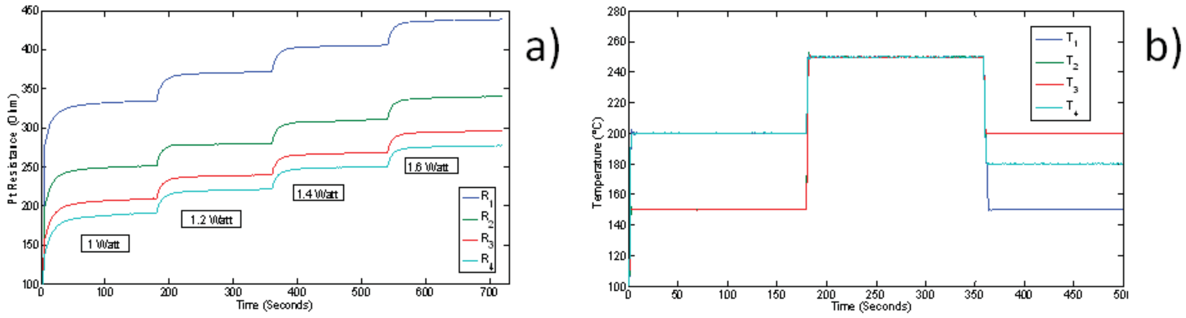

Figure 2. (a) Open loop operation; (b) Closed loop operation: temperature measurement

In figure 3 two examples of the measurement campaign results are shown: sensors are characterized in terms of electrical resistance response to NO_2 as a function of operating temperature (figure 3a,e).

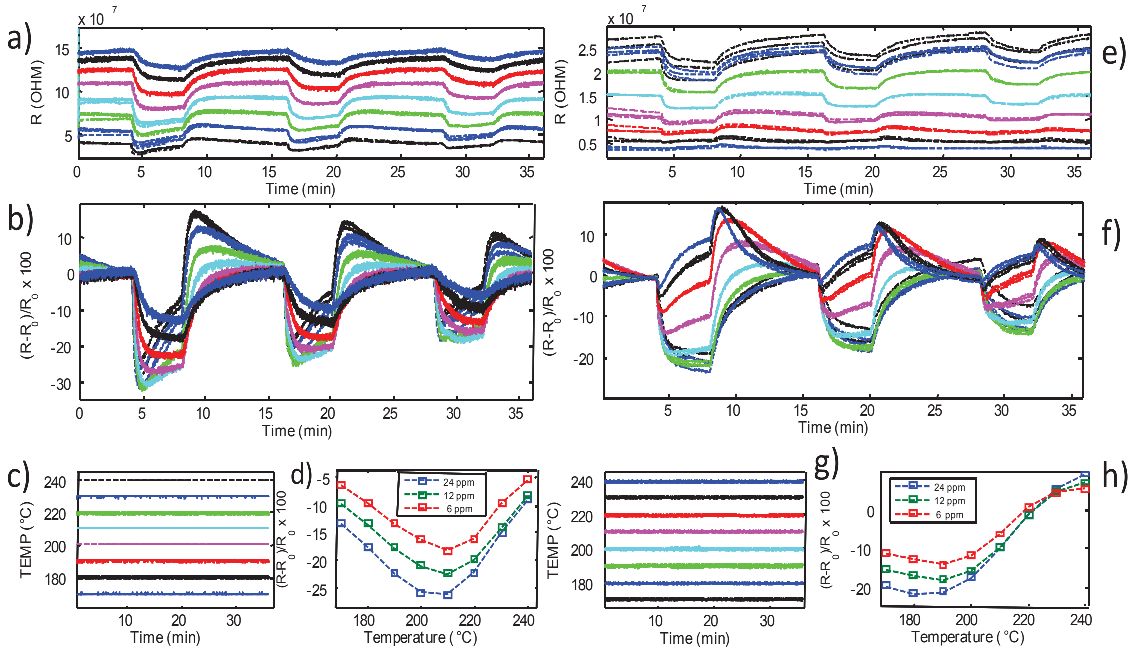

Figure 3. Automatic characterization of two sensors, raw and processed data

Each measurement is repeated 5 times in order to test the sensor stability, reliability and measurement repeatability and it is performed at a fixed temperature; eight different operating temperatures, from 170°C to 240°C, were used (figure 3c,g). A fixed total gas flow of 200 mL/min is set and the followig measurement protocol is used in order to asses the normalized response of the sensor (figure 3b): Nitrogen (N_2) for 4 min, a mixture of N_2 + 24 ppm NO_2 for 4 min, N_2 for 8 min, a mixture of N_2 + 12 ppm NO_2 for 4 min, N_2 for 8 min, a mixture of N_2 + 6 ppm NO_2 for 4 min, N_2 for 4min. R_0 represents the resistance in the carrier gas. In figures 3d and 3h responses at different temperatures and gas concentration are shown.

IV. Conclusions

In this paper a fully programmable system for automatic characterization of novel gas sensing materials is presented. It allows for accurately setting the measurement operating conditions in terms of environment gas composition, gas flow, humidity and temperature. Furthermore the system allows for performing tests in transient chemical conditions at fixed temperatures as well as tests in fixed chemical conditions, but variable temperature with arrays of 8 different sensors.

References

[1] G. Korotcenkov, "Metal oxides for solid-state gas sensors: What determines our choice?", *Mater. Sci. Eng., B*, vol. 139, pp. 1 – 23, 2007.

[2] A.Fort, M.Mugnaini, S.Rocchi, and V.Vignoli, "Surface state models for conductance response of metal oxide gas sensors during thermal transients," in *Chemical Sensors: Simulation and Modeling*, vol. 2: Conductometric-Type Sensors, G. Korotcenkov Ed., NJ: Momentum Press, 2012.

[3] A.Fort, M. Mugnaini, S. Rocchi, M. B. Serrano-Santos, R. Spinicci, V. Vignoli, "Surface State Model for Conductance Responses During Thermal-Modulation of SnO_2-Based Thick Film Sensors: Part II—Experimental Verification", *IEEE Trans. Instr. Meas.*,Vol. 55, n. 6, pp. 2107 – 2117, 2006.

[4] S. Bicelli, A. Depari, G. Faglia, A. Flammini, A. Fort, M. Mugnaini, A. Ponzoni, V. Vignoli, S. Rocchi, "Model and experimental characterization of the dynamic behavior of low-power carbon monoxide MOX sensors operated with pulsed temperature profiles", *IEEE Transactions on Instrumentation and Measurement*, Vol. 58, n. 5, pp. 1324 – 1332, 2009.

[5] A.Fort, S. Rocchi, M. B. Serrano-Santos, R. Spinicci, V. Vignoli, "Surface State Model for Conductance Responses During Thermal-Modulation of SnO2-Based Thick Film Sensors: Part I—Model Derivation", IEEE Transaction on Instrumentation and Measurement,Vol. 55, n. 6, pp. 2102 – 2106, 2006.

[6] A.Fort, M.Mugnaini, S.Rocchi, and V.Vignoli, "Surface state models for conductance response of metal oxide gas sensors during thermal transients," in Chemical Sensors: Simulation and Modeling, vol. 2: Conductometric-Type Sensors, G. Korotcenkov Ed., NJ: Momentum Press, 2012.

[7] A.Burresi, A. Fort, S. Rocchi, M.B. Serrano Santos, N. Ulivieri, V. Vignoli, "Temperature profile investigation of SnO2 sensors for CO detection enhancement", IEEE Trans. on Instrumentation and Measurement, vol. 54, no. 1, pp. 79–86, 2005.

[8] S. Bicelli, A. Depari, G. Faglia, A. Flammini, A. Fort, M. Mugnaini, A. Ponzoni, V. Vignoli, S. Rocchi, "Model and experimental characterization of dynamic behavior of low power Carbon Monoxide MOX sensors operated with pulsed temperature profiles", IEEE Transaction on Instrumentation and Measurement, Vol. 58, n. 5, pp. 1324 – 1332, 2009.

[9] A. Burresi, A. Fort, S. Rocchi, B. Serrano, N. Ulivieri, V. Vignoli, "Dynamic CO recognition in presence of interfering gases by using one MOX sensor and a selected temperature profile", Sensors and Actuators B, vol. 106, pp. 40-43, 2005.

[10] A.Fort, M. Mugnaini, S. Rocchi, V. Vignoli, E. Comini, G. Faglia, A.Ponzoni, "Metal-Oxide nanowire sensors for CO detection: Characterization and Modeling", Sensors and Actuators B, Vol. 148, n. 1, pp. 283-291, 2010