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Exploitation of a low-cost electronic system, designed for low-conductance and wide-range measurements, to control metal oxide gas sensors with temperature profile protocols

A. Ponzoni[a,*], A. Depari[b], E. Comini[a], G. Faglia[a], A. Flammini[b], G. Sberveglieri[a]

[a] CNR-IDASC SENSOR Lab and Department of Chemistry and Physics, University of Brescia, Via Branze 38, 25123 Brescia, Italy
[b] Department of Information Engineering, University of Brescia, Via Branze 38, 25123 Brescia, Italy

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ABSTRACT

This work is the continuation of two previous works: in the former we developed a WO_3 based gas sensor featuring high sensitivity to NO_2 but with the drawbacks of low conductance values (below 1 nS) and long recovery times (over 20 min); in the latter we developed a low-cost control electronic circuit suited to measure a wide range of conductance values (10 pS–100 μS).

Here, we use this electronic system to control this WO_3 sensor according to temperature profile protocols, with the aim to show the possibility to handle such low conductance devices by means of cheap instrumentation, featuring at the same time reduce response times and a degree of selectivity arising from the temperature profile protocol. In particular, we focus on two target applications: detection of NO_2 and detection of reducing gases, namely ethanol and methane, in different humidity conditions, showing the usefulness of time constants extrapolated from the response dynamics for the purpose.

1. Introduction

Metal oxide chemiresistors have attracted a large interest due to their high sensitivity to a broad range of chemicals as well as to the possibility to prepare devices featuring reduced size, weight and power consumption by means of cheap methods of preparation.

These devices have been the subject of several works dedicated both to the understanding of their basic mechanism and to the development and optimization of sensing layers as well as the exploitation in different applicative fields.

Material scientists dedicated to the development of sensing layers featuring a wide range of sensing properties through the optimization of the oxide structure, such as the grain size, morphology, porosity, chemical composition. For example, by properly adjusting synthesis parameters of WO_3 layers, high sensitivity to oxidizing gases can be obtained at room temperature [1]. The n-type sensing properties of pure TiO_2 can be modified in a p-type sensing material by the addition of Cr [2].

In order to fully exploit the new materials while keeping cheap the device use, the possibility to read the sensor electrical signal through low-cost readout electronic circuits is important as well. This often contrasts with some papers reported in the literature. It is the case, for example, of WO_3, which is widely recognized as one of the most suited oxides to detect NO_2, but its low conductance often falls below the Nanosiemens, especially during exposure to NO_2 [1,3–5]. These values are out of range for most of cheap electronic readout systems and expensive picoammeters are necessary to measure the sensor signal. Furthermore, the WO_3 sensitivity to NO_2 is optimized at low sensor temperature (usually below 250 °C), where interfering effects induced by humidity are enhanced [6] and the sensor response (and recovery) dynamics are slowed down [3].

To this aim, we have developed a low-cost readout electronic system suitable to perform fast measurements (every 10 ms) over a wide range of values (10 pS–100 μS) [7]. In a previous work, we used a first prototype of the system to control an array of four metal oxide (MOX) based chemiresistors. Working with isothermal protocols, this electronic nose was used to discriminate key-aromas developed during the bread baking process [8].

The electronic system has been further developed to control the sensor temperature, with the aim to develop an autonomous device (sensor and electronics) fulfilling the requirements of reduced cost, fast readings, wide range of measurable conductance [9,10]. In this way, it is possible to obtain a degree of selectivity using a single sensor working with temperature profile methods. These methods are based on the temperature dependence of the oxide–gas interaction and use temperature profiles to induce complex interaction dynamics. So far, the whole conductance profile along time can be exploited to extrapolate chemically sensitive information (features) [11–13].

* Corresponding author at: CNR-IDASC SENSOR Lab and Department of Chemistry and Physics, University of Brescia, Via Valotti 9, 25133 Brescia, Italy.
Tel.: +39 030 3715707; fax: +39 030 2091271.
E-mail address: andrea.ponzoni@ing.unibs.it (A. Ponzoni).

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In this work, we use our recently developed control-system [9] to control a WO_3 based gas sensors working with temperature profile mode to detect NO_2 in air under different humidity conditions, showing the suitability of this sensing system (sensors and control electronics) to overcome drawbacks intrinsic in isothermal methods.

2. Experimental

2.1. Control and read-out electronics

An ad-hoc electronic circuit has been designed for the complete and flexible management of resistive chemical sensors, such as metal oxide devices. The system is therefore able to acquire the sensor value within the typical wide range of variation; moreover, the sensor heater handling is carried out, to provide the desired thermal profiles. Fig. 1 shows the front-end developed for the estimation of the sensor parameters; in particular, the sensor conductance G_S as well as a parasitic capacitance C_S, modelled in parallel with G_S, can be estimated with a very fast readout (10 ms). It is based on a conductance-to-time conversion (CTC) scheme, which allows a wide range of conductance to be estimated without using scale factors [14]. This is possible because the duration of time intervals is easy to be estimated even in a wide range, for example by means of microcontrollers or digital counters implemented in programmable logic devices (PLD). In Fig. 1, the combination of the integrator *Int* and comparator *Comp* generates a pulsed signal, the duration T_p of which is related to the sensor conductance G_S. However, since scale factors are not adopted, the measuring time can be quite long with very low conductance values (e.g. on the order of tens of seconds with $G_S \sim 100$ pS); such a long measure time cannot be accepted for application in which fast phenomena have to be observed. To obtain a short measuring time, an interpolation method, by means of the least means square (LMS) algorithm, is used whenever the CTC approach requires a longer time to be accomplished. This is achieved by sampling the output signal V_o of the integrator *Int*, by means of an A/D converter and by applying the LMS interpolation to the acquired digital samples. In such a way, the time characteristics of V_o, and as a consequence G_S, can be estimated in a constant and fixed time interval, determined by the number of samples needed to achieve the desired accuracy for the LSM algorithm application. The switch SW_R allows to properly start and restart the measure, thus assuring the regular and fixed measuring time (10 ms) to be respected. The system architecture is designed to operate with a constant sensor bias voltage; in this way, effects of the presence of an in-parallel parasitic capacitance C_S are eliminated. However, for diagnosis purposes, the system is able to provide an estimation of C_S by temporarily varying the sensor bias voltage by means of the switch SW_C. More details about the system operating principle can be found in [14].

Fig. 2 shows the block scheme of the complete system, detailing the stage devoted to the thermal management of the sensor [9]. This circuit has been specifically designed to operate in a synchronous way with the system subpart handling the sensor value acquisition, also shown in the same figure. The sensor heater is driven by a user-programmable voltage V_{tot}, furnished by means of a digital to analog (D/A) converter followed by a current boost. In this way, relatively large values of current can be provided to the sensor, thus allowing high sensor operating temperature to be reached. The current I_h flowing through the sensor heater is estimated by means of the voltage drop V_{sh} on the shunt resistor R_{sh}, and then acquired by means of an analog to digital (A/D) converter. Thus, the actual heater voltage V_h can be easily computed and, together with the estimated value of I_h, allows both the heater resistance R_H and the heater power P_H to be reckoned. Every measuring cycle (10 ms), a new value of V_{tot} can be provided and a new estimation of the heater parameters is carried out, in a synchronous way with G_S and C_S estimations. A control loop on the sensor temperature can therefore be implemented, to keep constant the sensor operating conditions and have more reliable and repeatable measurements. Moreover, it is possible to apply various thermal profiles and simultaneously finely track both the sensor and the heater behaviour; in this way, different sensor operating conditions can be explored and analysed.

Finally, collected data are sent every cycle via a serial link to a PC, where a human interface application in LabVIEW environment allows the user to set the measurement parameters, to create the desire thermal profile and to save the sensor data for off-line analysis.

2.2. Gas sensor

The WO_3 layer used as sensing element has been prepared over a 2 mm × 2 mm × 0.25 mm alumina substrate by a modified thermal evaporation method detailed in [3]. Two interdigitated electrical contacts spaced by 200 μm were deposited by sputtering DC over the oxide layer. The device was provided by a Pt meander (deposited by sputtering DC) acting both as heating element and temperature probe on the substrate back side.

2.3. Gas-sensing measurements

Measurements were carried out by flow through method working with a constant flow of 300 sccm in a thermostatic sealed chamber at room pressure under controlled humidity conditions (RH = 30–50% at 20 °C). Controlled gas mixtures were obtained by using mass flow controllers mixing flows from certified bottles.

Before each measurement, the atmosphere composition has been stabilized for about 20 min, in order to avoid troubles arising from the test chamber filling and purging times, corresponding to about 3 min.

3. Results

3.1. Detection of NO_2

3.1.1. Response parameters and selectivity

In a previous work [3], we have developed a method to synthesize a WO_3 by means of thin film technology (a modified thermal evaporation) featuring high sensitivity to NO_2, with response about six times higher than WO_3 layer prepared by sputtering ($G_{gas}/G_{air} = 18$ and $G_{gas}/G_{air} = 3$ respectively to 0.2 ppm of NO_2). Besides these potentialities, the thermally evaporated layer features a very low conductance baseline (around 1 nS) at the optimal working temperature for NO_2 detection (100 °C) and slow recovery kinetics: the sensor conductance takes more than 20 min to recover the baseline value (within 70%) after the NO_2 injection has been switched off.

Temperature profile protocols have the potentialities to overcome these drawbacks while keeping the mentioned advantage.

The adopted protocol consists in a squared wave applied to heating element, with period of 30 s, composed by a heating transient of 10 s and a cooling transient of 20 s. The voltage levels are 1.41 and 2.60 V respectively, which cause the sensor to span the working temperature from 170 to 330 °C. According to results obtained during our previous investigation in isothermal conditions, this temperature range spans from temperature low enough to have high sensitivity to NO_2, to temperature high enough (330 °C) to fasten reaction kinetics.

Fig. 3 shows two periods of the square wave applied to the heating element, together with its resistance (R_H) and temperature (T_H) variation with time, and the sensor conductance G_S measured in