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Ultimate response dynamics achieved with gas sensors based on self-heated nanowires

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Abstract

Bias current applied to conductometric gas sensors consisting of individual metal oxide nanowires can be used to heat them up to the temperature necessary for sensing. This approach in combination with the good sensitivity and stability of metal-oxide nanowires, can be used to develop prototypes with low power requirements (few tens of microwatts). Here, we present new sensors devices based on this approach that display fast dynamic performance only limited by the gas-solid interaction kinetics.

Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

In the last years, intensive research efforts have been undertaken to fabricate innovative nanowire-based devices [1]. In particular, the development of conductometric gas sensors consisting of individual metal oxide nanowires has been a fruitful field of research, that has given rise to promising prototypes with some performances superior to their micro-counterparts [2]. The small size of these systems facilitates that bias current applied during the measurements heat them up to the working temperature necessary for sensing some gas species [3]. This effect is directly related to dissipated power in their inside by Joule effect [4], and provides an excellent tool to modulate the effective temperature of these nanowires.

In this work, we present an experimental approach which combines the good sensitivity and excellent stability attributed to metal oxide nanowires, with the low power requirements (only a few tens of microwatts) necessary to operate nanowire-based gas sensors using the self-heating operation mode. Here, we report that these proof-of-
concept devices display fast dynamic responses only limited by the gas-solid interaction kinetics, since most of the interfering gas diffusion processes—typical of porous film-based sensors—are eliminated.

2. Motivation and Results

The response of conductometric metal oxide gas sensors is strongly determined by the heating/cooling dynamics of the substrate, and the gas diffusion through the pores of the sensing layer [5]. In the last years, the design optimization of microhotplates made possible overcoming the first limitation and thus, thermal dynamic time constants in the range of tens of milliseconds were attained [6]. Nevertheless, gas diffusion remains as an unsolved problem. For this reason, response and recovery time constants of sensors are still well-above the second range [7]. Using individual nanowires to build up sensors completely eliminates this undesired effect because of their geometry [8]. Moreover, their tiny mass facilitates fast self-heating and cooling effects, with dynamics comparable with those observed using microhotplates [2]. Here, we present proof-of-concept devices based on individual SnO₂ nanowires (Figure 1) [3], which are thermalized with self-heating effect [4], displaying response and recovery times only limited by the chemical kinetic response of the sensing material.

![Fig. 1. Micrograph of one of the nanowire-based devices. Individual nanowires were electrically contacted in 4-probes configuration with the help of a Focused Ion Beam (FIB) instrument.](image)

![Fig. 2. Heating and cooling transient of the nanowire resistance in pure N₂. Current values \( I_m = 0.1 \) nA and \( I_m = 100 \) nA were applied to set the wire temperature to \( T = 25^\circ C \) and \( T = 300^\circ C \), respectively. Single exponential decay laws were fitted to the experimental records to estimate the thermal time constants.](image)
The resistance modulation of nanowires in pure nitrogen (N$_2$) due to Joule effect was used to determine their thermal response. According to the experimental data, heating and cooling dynamics followed exponential decay laws with time constants below 10ms (Figure 2). This demonstrates that pulsed heating stimuli up to 100Hz in frequency can be applied to these devices. It is noteworthy that this result is comparable with those obtained with standard technologies (i.e. microhotplates), despite the here-presented technique is still in its infancy.

Fig. 3: Response $R/R_0$ (where $R$ is the wire resistance and $R_0$ is the reference value at room temperature $T = 25 ^\circ C$) of our SnO$_2$-nanowires-based devices, exposed to two steady concentrations of (a) CO and (b) NO$_2$, operated in pulsed self-heating mode. (c) Summary of the response times obtained at different temperatures. Thermal response times of the devices are also indicated as reference.
The dynamic response of these devices towards oxidizing and reducing gases was evaluated in detail (Figure 3) by applying heat pulses through the bias current to activate the response towards different gases. These first prototypes needed only 30 ms before reaching a complete stabilization upon exposure to reducing species ([CO] = 500 ppm in air; T\textsubscript{opt} = 300ºC). Here, T\textsubscript{opt} indicates the temperature associated to the maximum response. On the other hand, 70 ms were necessary to observe the stabilization in oxidizing atmospheres ([NO\textsubscript{2}] = 5ppm in air; T\textsubscript{opt} = 175ºC). These results are two orders of magnitude faster than the reported ones for present technologies. It should be highlighted that stable responses were measured with all the heating pulses, showing that accurate estimations of the gas concentration can be obtained applying very short pulses of current (100 ms); and opening the door to further reductions of power consumption in the future [3,9].

3. Conclusions

Conductometric gas sensors based on individual nanowires with ultra low power requirements necessary to be operated (only a few tens of microwatts) can be obtained if they make use of the self-heating effect produced by bias current. These devices exhibit faster dynamic responses in pulsed operation mode than their thin-film counterparts, since interfering diffusion processes are eliminated due to their geometry, and pave the way towards more efficient metal oxide gas sensors.

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A Spanish patent application (P200900334) related to the above disclosed features has already been filled [9].

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