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Short Communication

Smart control of chemical gas sensors for the reduction of their time response

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ABSTRACT

The objective of this paper is to show the first results obtained with a gas sensor made of Au-functionalized WO_3 nanoneedles working under a closed-loop control designed to reduce its time response. The average temperature applied to the sensor is modulated to keep constant the average surface potential of the sensing nanostructures. This is done by periodically monitoring the resistivity of the sensing layer and generating temperature waveforms that enforce the condition: constant resistivity of the sensing layer at a reference temperature. Changes induced by the target gases must be compensated by changes in the average temperature being applied to the sensing layer. This signal, the average temperature applied to the sensor, is the new sensor output.

1. Introduction

The interest in gas sensors based on monocrystalline metallic oxides (nanoneedle, nanotubes and nanocolumns) has been increased in recent years. These nanomaterials present very good properties since most of their atoms are located on the surface and, therefore, can interact better with the environment, thus enhancing the sensitivity of the sensors. They also have a high crystallinity, thus reducing the presence of damages in the inter-grain boundaries, are more stable than their polycrystalline counterparts and they present a well defined controllable surface (chemical composition and crystalline phase). On the other side, though, gas sensors based on these materials present a slow time response to changes in gas concentrations and may present unwanted long term drifts in their characteristics.

Measurements with this type of sensors are usually made in an 'open-loop' configuration. With this approach, the temperature of the sensing layer is set at the desired working point. Variations in gas concentrations generate changes in the concentration of the chemical species within the sensing layer, which result in changes in the resistivity of the sensing layer. Temperature modulations have been applied, thereby improving the selectivity of the sensors, but the time response still remains slow [1]. Extensive work has been done in the obtention of dynamic models [2,3]. It is widely accepted the necessity of using nonlinear models in order to describe the time evolution of the chemical reactions within the sensing layer. As a result, some works have used neural networks [4], probabilistic state estimation [5], reservoir computing [6], or Support Vector Machines [7].

The approach in this paper is to apply closed-loop control techniques that are often used in other fields [8,9], to control the average surface potential of the nanostructures. The control will keep this potential constant by adapting the average temperature profile of the sensing layer, which is the new output signal of the system. The final objective is to obtain a reduction of the time response of the sensor to changes in the target gases.

2. Closed-loop control

In order to design the control loop the first step is the analysis of the influence of temperature on the sensing layer. The nanoneedle conductance, according to potential barrier theory [10], is:

$$G = G_0 T^{-\frac{3}{2}} e^{-\frac{qV_S}{k_B T}} \quad (1)$$

where G_0 is a factor taking into account different parameters of the nanoneedle geometry and other electrical characteristics, V_S is the average surface potential, k_B is the Boltzmann constant and T is temperature. Other conduction models (diffusion theory or thermoelectronic emission theory) generate equivalent expressions. In any case, the conductivity of the sensing layer is a function of temperature and the average surface potential.

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The surface potential depends on the physisorption and chemisorption (and their inverse counterparts) of species within the surface of the sensing layer. The effective surface-charge density ultimately determining this surface potential, is the result of one or several chemical reactions taking place on the surface of the sensing layer. The surface potential is a function of the density of the occupied states and has the expression: $V_s = qN_s^2/(2\epsilon_r\epsilon_0 N_d)$, where $\epsilon_r\epsilon_0$ is the electrical permittivity of the semiconductor and N_s the density of the occupied states and N_d is the total density of surface states [11].

This means that changes in temperature generate changes in the sensing layer by two different mechanisms:

- The first one involves the potential barrier theory (or other conduction theories) and is a very fast process. Sudden changes in temperature generate almost instantaneous changes in the resistivity of the sensing layer by way of the explicit temperature dependence in expression (1).
- The second one is due to changes in the surface potential, V_S. The effective surface-charge density depends on the dynamics of the intrinsic and extrinsic surface states, which depend on the target gases in contact with the surface as well as on temperature. All these processes have a very slow time evolution [12].

The objective of the proposed control is to keep constant the average surface potential of the sensing layer by changing its average temperature. Fast temperature commutations will be used to measure periodically the resistivity of the sensing layer at a constant reference temperature. The proposed control will generate temperature waveforms that in average will tend to keep constant this surface potential. The new output signal of the sensor is, therefore, the average temperature of the sensor. By suppressing the change in surface potential, and hence the slow dynamics associated to this change, we expect to improve significantly the dynamics of sensor response and recovery.

3. Implementation

The implementation that has been made includes two control loops. The first one is used to set the desired temperature of the sensing layer and is based on sigma-delta modulation [8]. The topology of the second level control loop is shown in Fig. 1. It is also a sampled system. At any given time two possible temperatures are applied to the sensing layer: T_{high} or T_{low}. This is done by adequately changing the threshold of the first temperature control loop.

In this feedback loop, the value of the chemical resistor is used to set up the actuation on the device during the next clock cycle. During each clock cycle, only two possible temperature profiles are applied to the device: BIT0 or BIT1 (shown in Fig. 2). Both profiles have been designed to end at the same temperature, T_{high}, and the chemical resistance is measured at the end of each sampling period. With this approach, the feedback variable is the resistivity of the sensing layer measured at a constant temperature: T_{high}. In our experiments, the control loop feedback was designed for an oxidizing atmosphere and, therefore, the control increases (decreases) the average temperature if the resistivity of the sensing layer is below (above) the desired value, therefore applying a BIT1 (BIT0) temperature waveform during the next clock cycle.

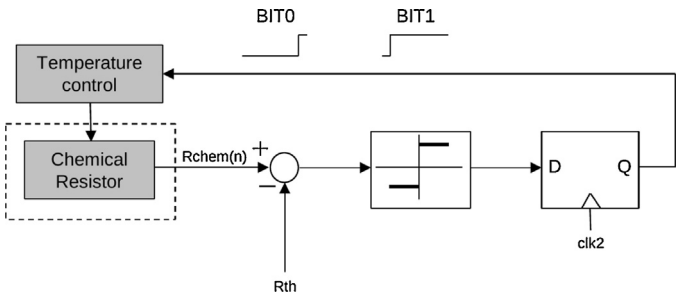

Fig. 1. Chemical sigma-delta modulator topology. At each sampling time, depending on whether the chemical resistance, measured at the reference temperature T_{high}, is below (above) the desired value, a BIT1 (BIT0) temperature waveform is applied to the sensor.

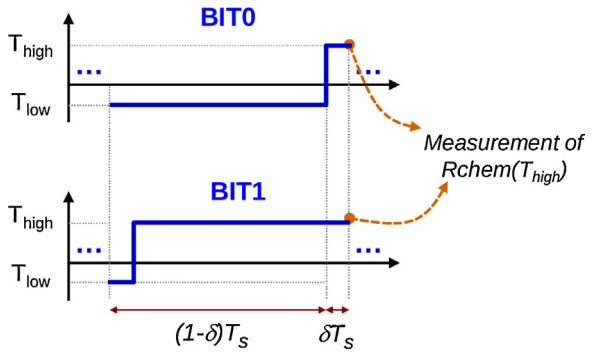

Fig. 2. Temperature waveforms applied during each sampling period of the chemical control loop.

4. Experimental results

The gas MEMS microsensors used in this work have active layers made of nanoneedles of WO_3 decorated with Au nanoparticles (see Fig. 3). The WO_3 nanoneedles functionalized with gold have been grown in a single step using localized aerosol-assisted chemical vapor deposition (AACVD), of tungsten hexacarbonyl (20 mg, $W(CO)_6$, Sigma–Aldrich, ≥97%) with tetrachloroauric acid trihydrate ((1 mg, $HAuCl_4{\cdot}3H_2O$, Sigma–Aldrich, 99.9%). These active sensing layers were grown on top of silicon MEMS membranes that comprise a pair of interdigitated gold electrodes and an embedded polysilicon resistor that performs the function of sensor heater [13,14]. The membrane has an area of 450 μm × 450 μm and the interdigitated electrode gap is 50 μm. The temperature coefficient of the polysilicon resistor is 6.79e−4 K^{-1}. By continuously monitoring the value of this resistor it is possible to estimate the time evolution of the temperature of the membrane of the sensor.

The sensing layer consists of a mesh of randomly oriented, single crystalline, tungsten oxide nanoneedles decorated with gold nanoparticles. The diameter of nanoneedles ranges between 60 and 120 nm and their length is about 6 microns. The average diameter of gold nanoparticles is 7 nm. More details on the morphology and composition of the film can be found elsewhere [15]. The morphology of the sensing layer is shown in Fig. 3.

4.1. Open loop characterization: fast and slow time scales

The objective of this section is to experimentally analyze how a change in the average temperature of the sensing layer generates a change in its resistivity. To this effect several experiments have been performed on which the value of the temperature of the sensing layer, determined by the value of the polysilicon resistor, is switched between two possible values (T_{high} and T_{low}). In a first experiment the sensor is kept a 10% of the time at the T_{high} and 90% at T_{low}. In a second experiment, the percentages are exchanged. In both cases, the repetition frequency of the pulses was 2 Hz. The temperature actuation waveforms for the first case can be observed in Fig. 4. The corresponding values taken by the chemical resistor