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Surface Ionization on Metal Oxide Gas Sensors

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Abstract:
In this work we present the development of surface ionization (SI) gas sensors with planar layout based on bundles of nanorods. We exploit a simple method, compatible with planar deposition techniques, to integrate the layer of nanorods into the functional device. The comparison between the same device provided and not provided with the nanorod layer shows that the measured signal arises from nanorods and not from the Pt electrodes. We further show that the adopted configuration and the exploitation of the nanorod morphology allow to reduce the working temperature from 600-900 °C to 300-400 °C and the voltage bias form 10000 V/cm to 1500 V/cm with respect to the traditional vertical layout.

Key words: Nanowires; Metal Oxide; Surface Ionization; Chemiresistors

Introduction

Metal oxide gas sensors have been widely studied in literature and exploited at industrial level thanks to their high sensitivity to a broad range of chemical compounds, the cheap methods of fabrication and the compatibility with silicon technology. Furthermore, their reduced weight, size and power consumption, which allows the development of portable instrumentation and/or the use in sensor networks.

Beside these potentialities, metal oxides suffer the reduced selectivity and not yet satisfactory long time stability.

Concerning selectivity, the most adopted solution is the electronic nose system: a sensor array with a pattern recognition software handling its collective response. To increase the variety of metal oxides that can be exploited in such systems, different approaches have been developed, such as, for example, materials based on doped, catalyzed or mixed oxides [1]. Other focused on the development of materials with controlled morphologies such as layers with pore size enabling the selective diffusion of molecules [2] or single crystalline nanowires [3, 4].

Recently, approaches based on novel sensing mechanisms, namely surface ionization, have been considered to exploit the potentialities offered by nanotechnology and nanostructured materials.

Surface ionization (SI) consists in the formation of positive and negative ions in the course of thermal desorption of molecules [5]. This working principle was traditional exploited in a vertical configuration, using a warm material (metallic or a metal oxide), where the gas adsorbs and ionizes, and a high electric field to extract ions and accelerate them toward a suspended electrode. High

temperatures, usually between 600 and 900 °C, and high electric fields, around 10000 V/cm, are necessary to activate these processes [5, 6]. Enhanced sensitivity has been observed using metal oxide layers with nanowire (nanorod) morphology, ascribing such an improvement to the nanowire structure, namely their high crystalline quality and their nanosized diameter, which ease the concentration of high electric field at their surfaces for ion extraction [6].
SI devices based on single nanowires have also been developed exploiting a planar layout with the single nanowire facing a Pt counter-electrode [7]. Results showed that this configuration can work at reduced temperature and at lower voltages with respect to traditional SI devices; nevertheless, it requires the use of advanced lithographic techniques such as Focused Ion Beam (FIB) to properly contact the single SnO_2 nanowire and is thus hardly exploitable at an industrial level. So far, strategies overcoming this technological gap are still need. In the present work we present our results on the development of SI devices based on horizontal layout but using a preparation method suited to directly deposit the oxide layer (based on a bundle of nanowires) over the functional substrate.

Experimental

In this work we focused on CuO nanorods.

Nanorods were prepared using a simple thermal oxidation method, consisting in a controlled oxidation of a thin copper layer inside a tubular furnace in a controlled atmosphere. This method feature the advantage of easing the selective growth the nanorods, just pattering (for example with shadow masking technique) the deposition of the metal film. The nanorods grow only where there is the copper layer. The thin metal copper layer is deposited via sputtering from a copper target. As expected the sputtering time has effect on the layer thickness, but we find out that the sputtering temperature changes the morphology of the copper metal layer and has effect also on the nanorods growth. After the thin layer deposition, samples are cleaned in air plasma for 5' at 15 W, to remove the very thin copper oxide layer that it's always present due to the reactivity of copper in air. After the plasma etching, samples were oxidized inside a tubular furnace for 15 hours at the temperature of 400 °C in an atmosphere composed by 80% O2 and 20% Ar.

The morphology of the obtained CuO layers is shown in Fig. 1. The CuO (Tenorite) phase was identified through XRD measurements.

Sensors were prepared using a 2mm x 2mm alumina substrate, according to the layout shown in Fig. 2, where the L-shaped electrodes are used to bias the oxide layer and the Pt meander is grounded and used as counter-electrode.

In order to identify the measured current as an effective ionization current, additional sensors, with the same structure but not featuring the oxide layer, were also prepared. In the following, CuO and Pt will be used to refer to the former and the latter device respectively.

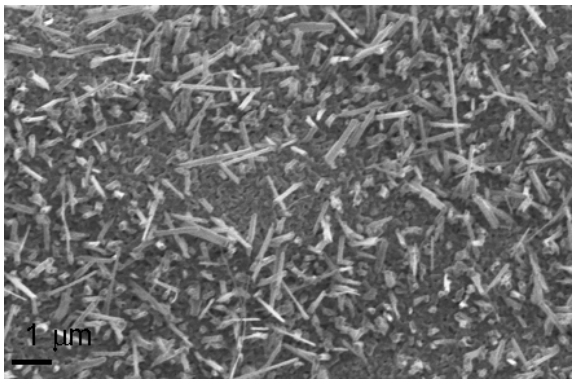

Fig. 1. SEM image of the CuO nanowire layer.

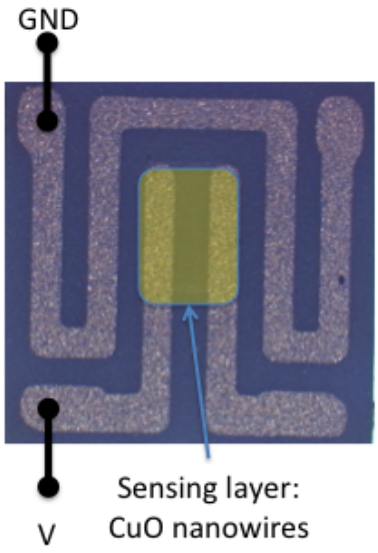

Fig. 2. Sensor layout for surface ionization measurements with planar configuration.

Gas sensing measurements were carried out in a stainless steel chamber under controlled humidity and temperature conditions. Atmosphere composition was controlled by

means of mass flow controllers balancing flows coming from certified bottles.

Results

The first step to develop SI devices based on planar layout is to prove that the signal comes from surface ionization phenomena instead of leakage current or other undesired effects.

To this aim, the sensor temperature was tested in the range 200-550 °C and the bias voltage in the range 1-300 V (corresponding to an electric field of 50-15000 V/cm).

Despite results obtained with SI devices designed according to the vertical configuration can provide a useful reference, phenomena in planar configurations are likely to be much more complex. In a planar configuration, both electrodes are heated at the same temperature (while in the vertical layout the counter-electrode is suspended over the heated device and is thus at a lower temperature), so that they can be both active in producing SI currents. Also, with a planar layout, ions generated over the electrode surface does not travel in air to reach the opposite electrode but are more likely to travel over the substrate surface.

So far, SI currents have been identified looking for asymmetries with respect to the bias voltage, which should arise in the CuO sensor (due to the facing of CuO and Pt electrodes) and not in the Pt sensor (due to the facing of two Pt electrodes).

As an example, responses to acetone and ethanol obtained at the senor temperature of 350 °C, with a voltage bias of +30 V are shown in Fig. 3 (a). The same measurements have been repeated with a bias of –30 V, Fig. 3 (b).

It is evident for these results that when the CuO sensor is biased with +30 V, it exhibits reliable responses to acetone (response amplitude increases with increasing the gas concentration). Differently, with a negative bias it shows some weak oscillations that disappear with time. The Pt sensor does not exhibit reliable responses, neither when positively nor when negatively biased. In both cases, it shows weak oscillations, with amplitude not related to the gas concentration, suggesting that SI is not activated in this device. The Pt layer feature indeed a compact structure that requires a much higher temperature and electric field to activate the SI signal with respect to layers with nanorod morphology [6].

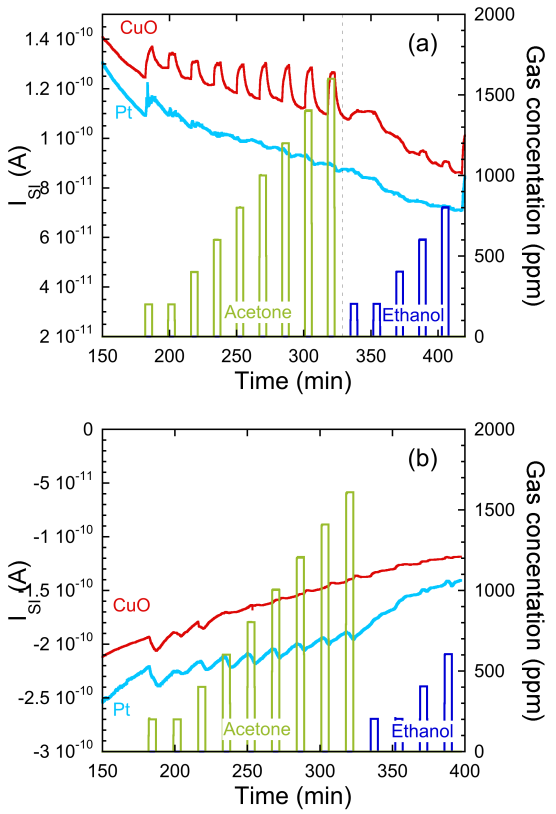

Fig. 3. Dynamic response of the CuO and Pt sensors to different concentrations of acetone and ethanol. Results have been obtained heated devices at the sensor temperature of 350 °C and using a bias of +30 V (a) and – 30 V (b).

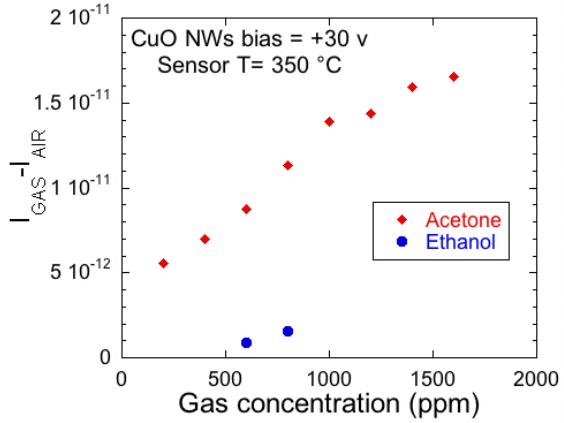

Fig. 4. Calibration curve of the CuO sensor to acetone and ethanol.

The response of the CuO sensor to different concentrations of acetone and ethanol are summarized in Fig. 4, showing the sensor calibration curve to these compounds. The much higher sensitivity to acetone than to

ethanol can be reasonably ascribed to its lower ionization energy (9.70 eV), compared to the 10.48 eV of ethanol, [8].

It's worth nothing that with the planar configuration, the working temperature and the voltage bias can be much lowered with respect to the vertical configuration. Optimal performance are here obtained at the sensor temperature of about 350 °C and with an electric field of about 1500 V/cm.

Conclusions

In this work we've presented a method based on the deposition of a metallic layer and its further oxidation to obtain metal oxide nanorods, showing in particular the suitability of the technique to prepare SI ionization devices with planar layout. Focusing on CuO nanorods, we've further shown that the nanorod layer is fundamental to produce the SI signal and calibrated the device toward two common chemicals such as acetone and ethanol.

These results are promising for the development of hybrid electronic nose systems, where the exploitation of different sensing mechanism, namely redo-ox reactions in chemiresistors and surface ionization phenomena in SI devices, would enhance the selectivity capability of the instrument.

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