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Low-cost fabrication of zero-power metal oxide nanowire gas sensors: trends and challenges

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Abstract

Self-heating of metal oxide nanowires when a measuring current flows through them allows simultaneously heating the metal oxide, which is required for correct gas sensing operation, and measuring the nanowire resistance change, which is achieved from the ratio between the voltage drop at its edges and the current injected by the source measurement unit. In this way a drastic reduction of the power consumption of the gas sensor down to some μW is obtained and, additionally, it simplifies the practical operation of the devices, but the required control electronics that assures the correct and stable current flow through the device becomes much more complex. In this work the degree of maturity of this almost zero-power consuming gas detection systems based on nanowires will be shown and some recent advances in the use of nanowires mats or carbon nanofibers will be presented.

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Keywords: metal oxide nanowire, gas-sensor, zero-power, self-heating, fabrication

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1. Introduction

In the last two decades, nanostructures, like nanowires, nanotubes, nanorods, …, have emerged as candidate components for the fabrication of future electronic devices. This is due, on the one hand, to the fact that their surface-to-volume ratio is large [1], which gives rise to pronounced interactions of the surface. On the other, the control over the growth conditions has allowed obtaining defect-fee and monocrystalline nanomaterials [2], which assures that their properties can be tuned for specific applications, and that the material can be reproducibly fabricated.

Semiconducting metal oxides have been used for over 40 years for the fabrication of gas sensors in different morphologies, especially thick or thin-films, which have demonstrated that general purpose and sensitive devices can be obtained. This lead to the creation of several companies selling these products, like Figaro, FIS, CCMOSSens, just to cite a few. To operate these devices, temperatures in excess of 150ºC are required to allow the desorption of the adsorbed gas species and due to the amount of material that constitutes the device, about 1W is required. With the use of suspended microhotplates with buried heater and integrated electrodes, it has been possible to reduce the power requirement by two orders of magnitude.

Metal oxide nanowires, thus, combine both benefits of enhanced surface effects and gas sensing properties. Furthermore, the use of individual nanowires as gas sensors has been proven to give similar results as their thick or thin-film counterparts [3], with the additional advantage that due to their reduced dimensions it is no longer necessary to heat the whole device and that only a reduced volume containing the nanowire should be enough. When operating as chemoresistors, the resistance value is obtained from the ratio between the injected current and the voltage drop across the nanowire and due to their ultrahin section, even for very low currents, important Joule heating can occur that might even melt the wire. But when a well-known and stable current is injected, a controlled heating occurs, the so-called self-heating, with simultaneously provides the required temperature and the resistance measurement [4]. In this manner the power consumption of such devices has been lowered to few tens of μW.

In this work we will present the results of our research in developing gas detection systems based on individual or mats of metal oxide nanowires for their use as ultra-low power consumption systems by using the self-heating phenomenon.

2. Experimental Details

SnO_2 NWs were synthesized following a method explained elsewhere [2] and which can be summarized as a vapour-liquid-solid process inside a chemical vapour deposition furnace using a molecular precursor $[Sn(O^tBu)_4]$. High resolution TEM images showed dislocation-free NWs with diameters ranging between 40 and 400nm depending on the experimental parameters of the process and lengths up to several tens of micrometres. The main growth direction of the grown nanowires was [100], with interplanar spacing in agreement with the rutile structure of SnO_2 [2]. The nanowires were removed from the substrates where they grew by sonication in ethanol or isopropanol and a drop of this solution was deposited onto oxidized silicon substrates or suspended microhotplates containing photolithographically prepatterned electrodes on their surface and in the case of the microhotplates, with buried electrodes.

The substrates containing the nanowires were afterwards inspected with the FEI Dual-Beam Strata 235 FIB instrument, equipped with an electron and a Ga^+ ion beam. For this, the electron beam was used that avoids damaging the nanowires and once correctly located, contact fabrication to the nanowire is carried out using a trimethylcyclopentadienyl–platinum ((CH3)3CH3C5H4Pt) precursor to deposit a Pt-containing amorphous carbon layer. The procedure for this contact fabrication method is explained in detail elsewhere [3].

Two- and four-probe dc electrical measurements were performed using a Keithley Source Measure Unit (SMU) 2602, the second source used to bias the buried heater of the microhotplates. Self-heating of the nanowires when a measuring the current flows through them allows simultaneously heating and measuring the nanowire, dramatically reducing the power consumption to some μW and simplifying the practical operation of the devices. However, the required control electronics that assures the correct and stable current flow through the device becomes much more complex. Based on this approach we have developed a portable detection system that uses a thermoelectric generator to provide the required operating power to both heat and read-out the gas sensing results [4].

Characterization of the contacted SnO_2 NWs towards different gases in synthetic air (79% N_2 and 21% O_2) have been carried out in a stainless steel chamber keeping a constant flow of 200 ml/min. Inlet gas flow has been controlled by Bronkhorst Mass-Flow Controllers and electrical measurements have been performed using a Keithley 2602A dual Source Measure Unit that allows the simultaneous control of the electrical parameters and the heating of the micro-membrane. Electrical measurements and flow control are managed by a specific own-developed Labview application.

3. Results and discussion

Fig. 1 shows an SEM image of one NW contacted in 4 point configuration using the methodology explained above. The 4 contacts are clearly visible. The time required for the fabrication was in the range of few hours. Similar fabrication methodologies were employed on the suspended microhotplates, but due to the charging of the membrane the quality of the contacts are not as good.

For temperature calibration purposes, the microhotplate represents an advantage due to the fact that the temperature of the nanowire can be independently calibrated using the buried heater as temperature source and measuring the resistance of the nanowire with an extremely low source current. Next the self-heating current is applied and, again, the resistance is measured and is calibrated against the previously measure value.

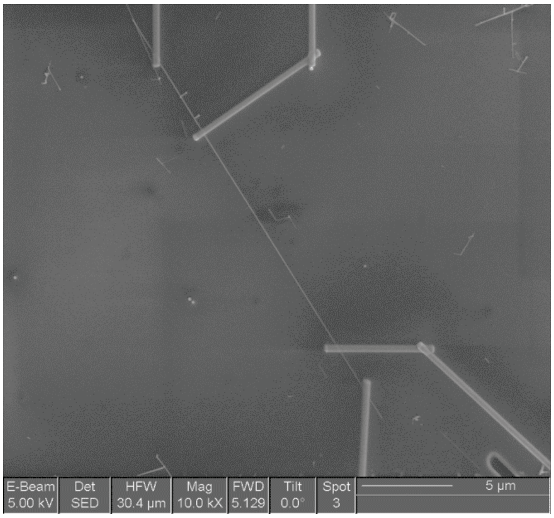

Fig. 1: SEM image of one SnO_2 NW contacted on top of a silicon substrate in 4 probe configuration.

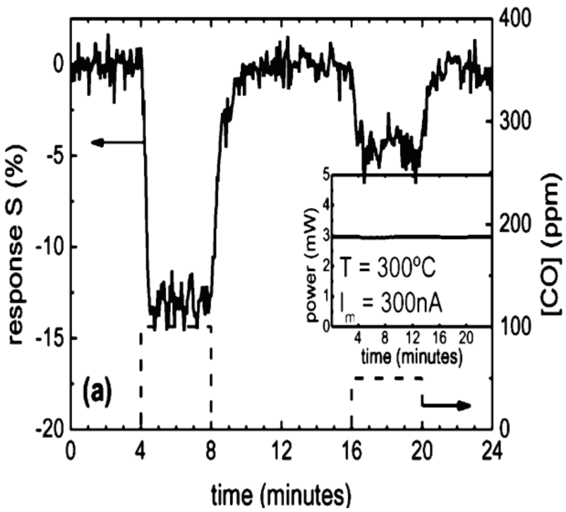

Fig. 2: Gas response of a single nanowire towards carbon monoxide, using 300nA as self-heating current, from which an estimate of 300ºC is derived.

When introducing a device containing an ultrathin nanowire as gas sensing element into the gas testing chamber under carbon monoxide flow in dry synthetic air and using a low current of 300nA, the estimated temperature reached is about 300ºC and is enough to clearly respond to this gas. The expected behavior for a reducing gas is observed (reduction of the resistance in the presence of gas) and the time response is small, of just some tens of seconds.

Fabricating contacts to individual nanowires presents the drawback of the reduced throughput of the technique and of the difference between two devices produced one after the other and, thus, other techniques are searched after. Among them, dielectrophoretic alignment of different metal oxide nanowire mats between two contacts on top of microhotplates and the use of the self-heating approach to measure the gas response has been reported recently [5], with good results. Of course, as a consequence of the use of a large amount of nanowires between the electrodes, the power consumption has increased by, at least, one order of magnitude to about 200µW. The value is still orders of magnitude smaller than the one required for heating the microhotplate. Additionally the presence of such a large amount of nanowires crossing between the electrodes strongly presents two important advantages: on the one hand, it reduces the risk of burning or damaging a device based on one single nanowire that may be caused by a current peak and, on the other, the current values required for this type of devices allow the use of much easier electronic circuitry, simplifying the operation of the devices.

Recently the self-heating methodology has been applied to carbon nanofibers with equally low power consumption, below 1 mW, much lower than what require the microhotplates [6]. In this case the process does not even require the external alignment of the nanostructures, as it uses randomly aligned nanofibers, even further simplifying the fabrication of the device.

4. Conclusions

Self-heating of metal oxide nanowires has been presented as a method for providing the temperature required for correct gas sensing operation while, simultaneously, measuring the resistance of the nanoresistor. The power required for the operation mode of these ultra low power consumption gas sensor devices is in the range of few tens of μW for single nanowire based devices. Furthermore the method has been extended to metal oxide nanowire mats and to randomly aligned carbon nanofibers that, with a higher power consumption but much lower than the one required by microhotplates, allows similar operation mode, circumventing the limitations of fabricating single nanowire based devices. The presented methodology represents an important step forward compared to commercial metal oxide gas sensing devices in comparison with single nanowire based devices.

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