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Locally grown SnO_2 NWs as low power ammonia sensor

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Abstract

Localized growth of SnO_2 nanowires on top of CMOS compatible micromembranes that incorporate a buried heater and prepatterned interdigitated electrodes has been achieved that presents the advantage that it allows to easily and directly integrate the advantageous properties of quasi-one dimensional structures in an advanced electronic device by a Vapor Liquid Solid (VLS) mechanism. A NWs based sensor of this type is characterized as a low power gas sensor towards NH_3 at different temperatures. Stable and reproducible response is obtained, that allows detecting concentrations below the time-weighted average exposure limit for 8h.

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Keywords: Nanowires; Metal-oxide; Gas-sensor; Micromembrane; Low-Power consumption.

1. Introduction

Research efforts devoted to the development of nanowires (NWs), nanorods and other nanostructures as a sensing part of advanced electronic devices are increasing due to the unique properties of these nanomaterials as a result of their high surface to volume ratio that are advantageous in many chemical and mechanical properties [1]. An

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important drawback for the use of nanostructures is the highly time consuming techniques required for the incorporation into functional devices. The fabrication process usually involves transfer of such nanostructures from the substrate where they were grown to the final prototype. A strategy to achieve more reliable device would include the localized growth of these nanostructures in the final electronic device, avoiding several steps that add uncertainty factors to the fabrication process.

One of the usual growth mechanisms of tin oxide nanowires is Vapor-Liquid-Solid (VLS), a one dimensional growth mechanism involved in the synthesis of several types of nanowires, carbon nanotubes and other nanostructures that are assisted by a metal catalyst [2].

Furthermore, the interaction between gas molecules and metal oxide is a surface mechanism which involves electronic transfer between the gas specie and either an oxygen vacancy or a chemisorbed oxygen from the metal oxide. One dimensional nanostructures, such as nanowires, are good candidates for this purpose due to their well-controlled physical and chemical properties. Typically these sensing properties require temperatures between 150 and 300ºC for correct operation, which can be achieved using micro-membranes with buried integrated heater and surface electrodes.

In this work, the localized growth of SnO_2 nanowires via the VLS mechanism directly on top of micro-membranes with buried heater and interdigitated electrodes has been carried out and the sensing characteristics of these NWs towards ammonia is reported and analyzed in this work

2. Experimental Details

SnO_2 NWs were synthesized using a non-continuous thin Au film of 2-5 nm, sputtered on top of a micromebrane, which acts as a growth seed of the VLS mechanism. The micromebrane is a closed structure fabricated by bulk micromachining that contains a buried heater and interdigitated electrodes on the top. These structures provide a temperature around 800°C in vacuum conditions that allows the growth of nanowires in a low power consumption CVD approach.

The precursor used was $Sn(O^tBu)_4$ and a temperature above 700ºC to activate nucleation of tin oxide NW via Au seed was kept. Growth is carried out in a quartz chamber in which the heater is polarized externally to achieve the required synthesis temperature in low vacuum conditions. These nanowires are therefore localized preferentially between the IDE contacts, requiring a power supply of 50 mW, an important reduction compare to a standard CVD furnace. No lithography masks are needed for the localized synthesis of NWs.

Characterization of the locally grown SnO_2 NWs towards NH_3 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. Experimental results

Homogeneous growth along the central part of the membrane is shown in Fig. 1 (a). The brighter area of the membrane highlights the profile temperature provided by the heater during the synthesis and remarks the area where NWs have been synthesized. High density and interconnected NWs are observed in Fig. 1 (b), where a clear contact with the metal electrode is also demonstrated.

SnO_2 is well-known material as a wide gap semiconductor material with a band-gap of 3.6 eV and whose resistance decreases when temperature raises. The resistance of the SnO_2 NWs based sensor decreases between room temperature and 200 °C, and increases for higher temperatures (see Fig. 1 (a)) as it has been reported for other SnO_2 based structures [3], due to the change of chemisorbed oxygen specie at the surface. Molecular oxygen (O_2^-) is chemisorbed at temperatures lower than 150 ºC approximately; as temperature increases molecular oxygen is dissociated in two atomic oxygen ions (O^-), which increases the resistance of the tin oxide nanowires. At higher temperatures atomic oxygen can be chemisorbed, sharing 2 electrons with an oxygen vacancy from the metal oxide (O^{2-}), providing an additional contribution to raise sensor resistance.

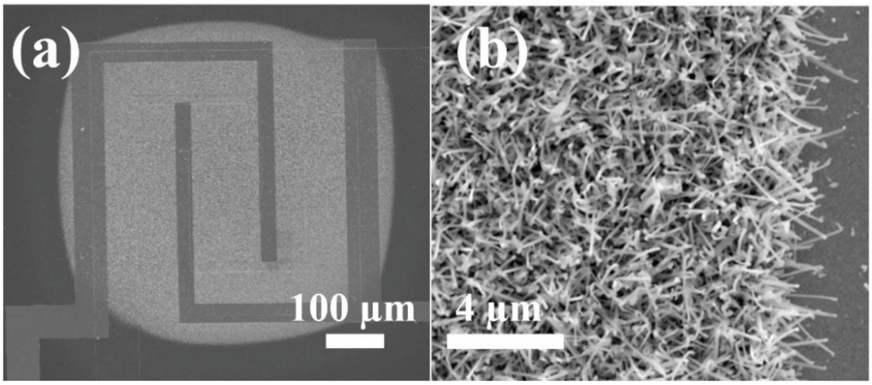

Fig. 1. (a) Top view of the micromembrane and the area where the NWs are grown (bright in the image); (b) SnO_2 NWs at the edge of the interdigitated metal electrode.

The behavior is also observed in the evolution of the resistance against different NH_3 pulses that are represented in Fig. 1 (b). Ammonia exposure time of 15 min and recovery time of 30 minutes was used in the gas test. The resistance decreases in the presence of NH_3, as expected for an n-type semiconductor gas sensor. Power consumption of the heater to provide 530°C is 46 mW. Similar power is required to achieve 700ºC during NW growth due to the low vacuum conditions that avoid the heat transfer by conduction; heat dissipation is performed uniquely via thermal radiation and thus, power dissipation is importantly reduced.

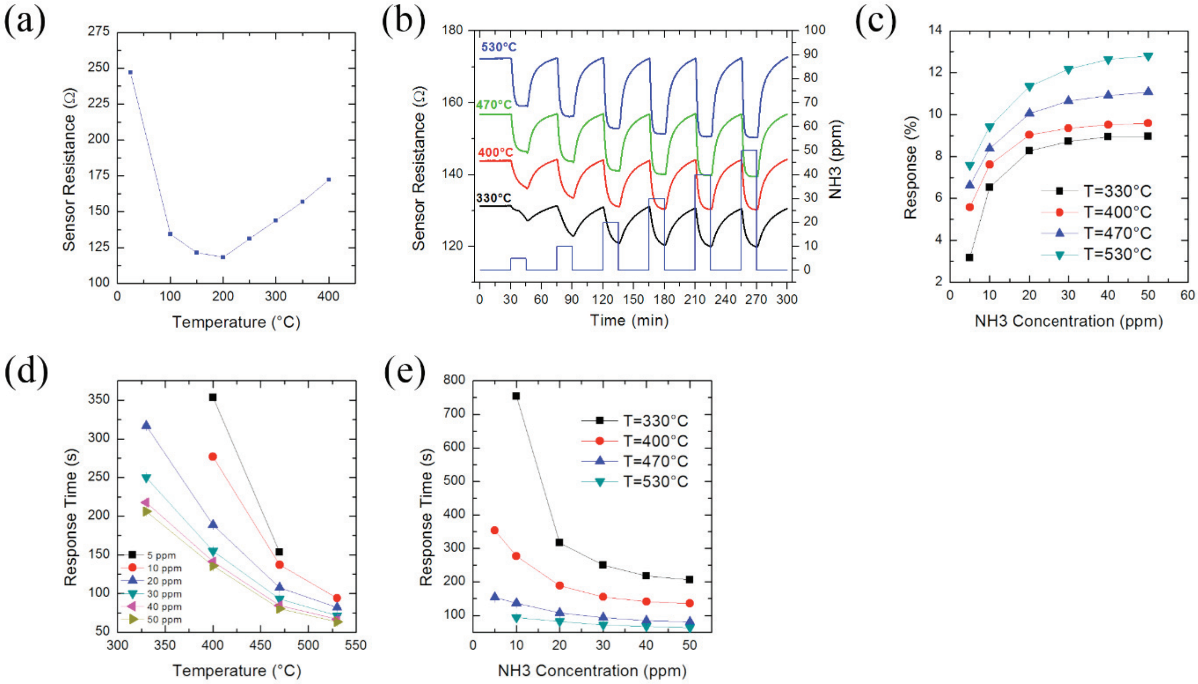

Fig. 2 (a) Resistance of localized grown NWs in function of temperature; (b) Evolution of sensor resistance against different concentration of Ammonia diluted in synthetic air at several temperatures; (c) Response of the sensor at different ammonia concentrations; Response time in function of (d) temperature and (e) NH_3 concentration.

The nanowire based sensor shows a stable baseline, and reaches a saturation in response around 30 ppm, a higher value than time-weighted average exposure limit for 8 h recommended by NIOSH (25 ppm) [4] as it is observed in Fig. 2 (c). In order to evaluate the gas sensing response, the following response is defined:

$$Response(\%) = \frac{R_{air} - R_{NH3}}{R_{air}} \cdot 100 \qquad (1)$$

Locally grown NWs have shown increasing response with temperature. The same behavior has been observed for other nanostructured SnO_2 materials [5]. Different response curve in front of temperature was observed in other works [6,7], where a maximum is obtained at a temperature around 200ºC, being reduced for higher temperatures. Sensing behavior in these works are limited to a temperature range lower than 350ºC.

Response time, defined as time from 10% to 90% of the final resistance value, is represented as function of temperature and ammonia concentration in Fig. 2 (d) and (e) respectively. The response time decreases with increasing temperature, achieving a response time of 63 s for 50 ppm at 530°C. Despite the sensor response is saturated for higher concentrations than 30 ppm of NH_3, the response time decreases with ammonia concentration up to 50 ppm.

In situ grown nanowires device has exhibited a large operational lifetime; prototypes have been operating towards toxic gas species for more than 3 months**,** demonstrating high durability and stability. These robust gas sensors here described present excellent characteristics for ammonia detection in indoor applications.

4. Conclusions

Locally grown tin oxide nanowires using the VLS method have been implemented in a reliable, low time consuming and low power consumption device supported on a micromebrane. NWs network have been characterized as ammonia sensor, showing capabilities to sense concentrations as low as 10 ppm of NH_3. Response time of 1 minute has been provided by the sensor, and long life operatibility has been proven after several months of measurements.

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