Electrospun nanobridges towards self-heated gas sensors with enhanced sensitivity

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Abstract. This paper reports the fabrication process of ZnO and GaN nanobridges by electrospinning, to be used for gas sensing applications. The main purpose is to produce single suspended fibers with their surfaces completely exposed to the gas for an enhanced sensitivity when compared with sensors fabricated with structures deposited on a substrate. In addition, the isolation from the substrate is highly favourable for a well-controlled current setting, taking advantage of self-heating effects to set appropriate temperatures for gas sensing. The current status of development of the nanobridge-based sensors is described in addition to a primary electrical characterization and the ongoing work involving the in-parallel fabrication.

1. Introduction

Semiconductor-based gas sensors have wide applications in medical diagnosis, environmental sensing and control applications. Recent research has been focused on nanostructured devices and new sensing concepts coming from nanoscience and technology. The reduction in grain size of nanostructured sensing materials, enables very high surface-to-volume ratios and therefore a wider area susceptible to gas exposures.

Gas sensing is possible thanks to the convection of electrical conductivity due to surface reaction such as oxidation or reduction caused by different gases. In detail, when the sensing material is exposed to a gas, a depletion of carriers is experienced in its grain boundaries and its properties are temporarily modified. Thus, the sensor response is highly dependent of the surface-to-volume ratio of materials because of the active centers and the defects existing on the surface layer of the materials. [1]

In comparison to conventional gas sensing devices such as those using bulk or thin films, one-dimensional nanostructures such as electrospun nanofibers have higher gas sensitivity due to their ultra-high surface-to-volume ratio. In the form of fibers, the transport properties could be strongly modified by reactions at grain boundaries and depletion of carriers. In this regard, Huang, \textit{et al}, made a comparison between a SnO\textsubscript{2} thin film and SnO\textsubscript{2} nanorods obtained from a plasma-treated thin film. The sensitivity was higher for nanostructures in a factor of 8. [2] Since this property was demonstrated, other gas sensors based on nanostructures have been studied. Different sensing metal oxides such as

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SnO$_2$, ZnO, WO$_3$, even conductive polymers like PEDOT-PSSA, have been used for sensing purposes of several gases including ammonia, hydrogen, nitrogen oxides, hydrogen sulphide, and CO, just to mention a few. [3-7]

Nevertheless, the nanostructures also carry on some disadvantages due to their dimensions, for example reduced lifetime. This problem is originated by the temperature gradients in the structure due to self-heating while it operates electrically [8, 9]. This issue is overcome by applying a well-controlled current value to an individual fiber [10], which allows setting an appropriate temperature to operate the fiber as gas sensor. This was already described by Prades et al using SnO$_2$ nanowires deposited by CVD. Their system exhibited responses nearly identical to those obtained with integrated microheaters, demonstrating the feasibility of self-heated gas sensors with ultralow power requirements. [7]

Our proposal is detecting the gases or vapours using individual electrospun nanofibers suspended as bridges. It is well known that electrospinning is an efficient, relatively simple and low cost way to produce nanofibers of several materials like metal oxides and conductive polymers, which have been already studied as single fibers for gas sensing [11, 12]. In comparison to these studies, where the fibers are deposited and sintered (in the case of metal oxides) over a substrate and usually are belt-shaped, our work leads to the enhancement of gas sensitivity since the exposed area is probably doubled. In addition, a suspended fiber avoids the significant thermal losses to the support, which allows a higher effectiveness of the power released in the structure. [9]

In order to prove the concept, we report the fabrication process of Zinc Oxide (ZnO) and Gallium Nitride (GaN) nanobridges. We also discuss some aspects related to their characterization, structural and electrical characterization. Finally, some guidelines for ongoing and future work are proposed.

2. Experimental procedures

Two stages are necessary to fabricate nanobridges by electrospinning. Firstly, the micromachining and preparation of substrates where the fibers are collected. Secondly, the deposition, sintering and nitration (only for GaN) of fibers.

Substrates were prepared from conventional 500-µm-thick silicon wafers. They are firstly covered by 400 nm of thermal SiO$_2$, deposited as electrical isolation layer. Then, the oxide and the substrate were etched by reactive ion etching (RIE) in order to make 10 µm-height structures with rectangular and squared patterns (see grid pattern in Figure 1). A photoresist of 2 microns was enough to serve as mask during RIE. The gaps between high-relief patterns are in the range from 5 to 50 µm. A similar process was performed to fabricate a uniform array of squared ‘mushrooms’ of 3x3 µm$^2$ separated 3 µm between them. SEM images of the substrates with some fibers deposited on them are shown in Figure 2.

![Figure 1. Grid pattern used to perform the array of high-relief structures.](image-url)
Once the substrates are prepared, GaN and ZnO nanofibers are deposited on them, using conventional electrospinning technique. First, a polymeric solution based on cellulose acetate (CA) was prepared to be used as carrier of the Zinc Nitrate (Zn(NO₃)₂) and Gallium Nitrate. The CA is previously dissolved in a 1:2 molecular weight ratio mixture of dymethylacetamide (DMA) and Acetone. CA is added to obtain a 20% wt solution.

In parallel to this, a 30% wt Zn(NO₃)₂ solution is prepared, using acetone as solvent (for ZnO), and 20% wt gallium nitrate solution was made using DMA instead acetone (for GaN). Each solution was mixed several hours with the polymeric solution in a volume ratio of 1:2. More details about precursor solution are presented in [13].

After deposition, proceeds the calcination of polymer and sintering of fibers. ZnO bridges are obtained by sintering the fibers at 600 °C in air for 3 hours, with a previous temperature ramp of 5 °C/min. Higher ramps were tried, but efficiency of bridges performing was low. Probably the forces and mechanics involved during sintering needs slow thermal variation. It is an issue that should be studied in order to improve the efficiency looking forward commercial nanofiber-based devices.

The GaN fiber is obtained by two stages: calcination/sintering and nitration. The first is made in nitrogen atmosphere at 500 °C during 3 hours with a previous ramp of 2.5 °C/min. Then, the atmosphere is changed to ammonia flowing at 40 sccm, the temperature is increased up to 900 °C at the same ratio and is hold for 3 hours. Once this phase has finished, ammonia atmosphere remains during cooling, which is controlled to be no higher than -5 °C/min.

3. Results and discussion
Electrospun nanobridges were successfully deposited as shown in figures 3 and 4. SEM characterization allows observing that ZnO bridges are highly granulated, which is favourable for gas sensing applications since the gas penetrates the structure and even larger area is exposed, however it could also make the bridges structurally weak and easy to break. The structures present a mean diameter of 700 nm, thinner fibers can be obtained if sintering time is longer or other parameters of electrospinning are controlled.

On the other hand, GaN bridges are thinner since the sintering process is longer and mainly because the temperature is higher. The mean diameter of fibers is around 150 nm, although 70-nm-fibers were observed. Although the GaN fibers present some granulation, in comparison to ZnO structures it is very low. The GaN fibers look more consistent and mechanically stronger, which make them suitable for longer bridges.
Figure 3. Electrospun ZnO nanobridges with lengths from 10 to 150 µm. A broken fiber is depicted to show that bridge performing is not a trivial process and temperature ramp affects sintering. Also paths of polymer fibers where the zinc was not sintered can be observed in the images. On right-bottom, a detailed image shows the high granulation of fibers.

Figure 4. (Top) Electrospun GaN nanobridges deposited on mushrooms. The fibers are visibly thinner than ZnO ones. (Bottom) A detailed image shows the granulation of GaN fibers. Although it is granulated, the appearance is of a solid wire.
Figure 5: SEM images showing two basic steps for electrical characterization: metal pads deposition (left) and biasing (right).

The electrical characterization was carried out using a source-measurement unit (SMU) integrated to a focused ion beam (FIB) chamber. In order to apply the voltage, metal pads are necessary. By FIB-assisted deposition of a thin film of Pt, the fibers are ready to be biased as figure 5 shows. Pads have dimensions of approximately 20x30 \( \mu \text{m}^2 \) and were deposited the closest possible to the edge of the high-relief structure for ensuring that results come exclusively from bridge. Then, tips connected to SMU are located on these pads and measurement is performed.

Figure 6 depicts the I/V curve of a single ZnO bridge with a diameter of 1.5 µm and length of 54.7 µm. Other fibers were tested and as can be expected, the resistance varies according to their dimensions.

Figure 6. I/V curve of a single ZnO bridge. The structure has an ohmic (resistor) behaviour, with resistance value of 4 MΩ.

4. Ongoing work

Single and suspended electrospun nanofibers were produced. The next steps involve the characterization of fibers as gas sensors. This process is preceded by the study of their thermal behaviour to test their self-heating capabilities and guarantee the temperature control by current-biasing. However, biasing each single bridge using FIB-assisted metal deposition is a highly time/money demanding technique. For this reason, the in-parallel metallization is planned to be done by stencilling. Details about this proposal can be found in [14].
5. References

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Acknowledgments

This research is partially funded by PENN-UPRH PREM (NSF-DMR-0934195).