From the fabrication strategy to the device integration of gas nanosensors based on individual nanowires

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ABSTRACT

In this paper the techniques required for the fabrication of gas nanosensors based on individual metal oxide nanowires on top of planar substrates will be presented. These prototypes are fabricated using sophisticated techniques, like focused ion beam, which lead to reliable devices but with a low throughput. Different fabrication strategies aimed at the mass production of such devices, combining bottom-up and top-down approaches, will be critically discussed, emphasizing their impact on the electrical behavior of the fabricated nanostructures and the limitations of the here-presented methodology.

Keywords: individual nanowires, metal oxides, gas nanosensors, microhotplates, dielectrophoresis

1 INTRODUCTION

Conductometric gas sensors based on metal oxides (MOX) amongst the most popular types of gas sensors used in alarm and control applications due to their low cost and good response towards toxic gas species, especially, on oxidizing and reducing gases [1]. In the last years, significant research efforts have been devoted to extend their fabrication to the nanoscale, using nanowires (NWs) as building-blocks, because of their excellent sensing properties related to the high surface-to-volume ratio and to the perfection of their crystalline structure. At the same time the reduced size of the materials requires the use of sophisticated high-resolution contact fabrication methods, which leads to a low throughput process. Research is carried out in searching alternatives or additional fabrication techniques that increase this throughput and that can be used on large surfaces, trying to make them compatible with microfabrication processes. In this work some of these techniques will be presented and discussed.

2 EXPERIMENTAL

Single crystalline, defect free SnO_2 NWs, with a rutile crystalline structure and radii between 20 and 200 nm, are synthesized by chemical vapor deposition of a molecular precursor [2]. Some of these NWs are removed from the substrate and dispersed in different solutions (typically ethyleneglycol), sonicated, and a drop is put over the surface of a SiO_2/Si substrate with photolithographically pre-patterned microelectrodes. The as-dispersed NWs are electrically contacted using a FEI Strata 235 Dual Beam focused ion beam (FIB) instrument, equipped with a $C_9H_{16}Pt$ injector, that allows to deposit a Pt-containing material. The detailed procedure for this contact fabrication method is explained in detail elsewhere [3] and consists in the sequential deposition of the Pt nanostripes stripe using the focused electron- and ion-assisted deposition (FEBID and FIBID, respectively), as shown in figure 1. *dc* electrical measurements are carried out using a Source Measure Unit, keeping the sample at temperatures of about 200-350ºC (473-623K), which are required for the correct operation of the device as gas sensor. Pulses of CO or NO_x gases of different concentration and duration mixed, with dry synthetic air, are introduced in the measuring chamber that contains the sensor and the resistance change measured.

For the alignment of the NWs, dielectrophoresis (DEP) experiments are carried out. For this, a special electrode layout has been fabricated on a SiO_2/Si substrate, which ensures a high electric field between the electrodes (figure 2). For these experiments, the NWs are dispersed in ethanol and a drop is placed on the substrate while AC-voltages of varied amplitudes and frequencies are applied and maintained until the full evaporation of the solvent.

Suspended microhotplates (MHPs), with lateral sizes of about 100µm, on which interdigitated Pt electrodes and buried Pt heaters are integrated, are fabricated using surface micromachining techniques. The same dispersion procedure as on standard SiO_2/Si substrate is used to place the NWs on the substrates for their contacting.

3 RESULTS AND DISCUSSION

3.1 Standard substrates

Figure 1 shows the result after the use of the contact fabrication strategy, consisting in the inspection of the sample using the SEM and once a NW is found, FEBID is used to deposit Pt nanostripes on top of the NW and, afterwards, the contacts are extended towards the prepatterned pads by FIBID because of the lower resistivity of the latter. In this particular example, 4 contacts have been fabricated to be able to perform 4-point probing experiments for basic characterization purposes, due to the high contact resistance between the Pt nanostripes and the NW [3].

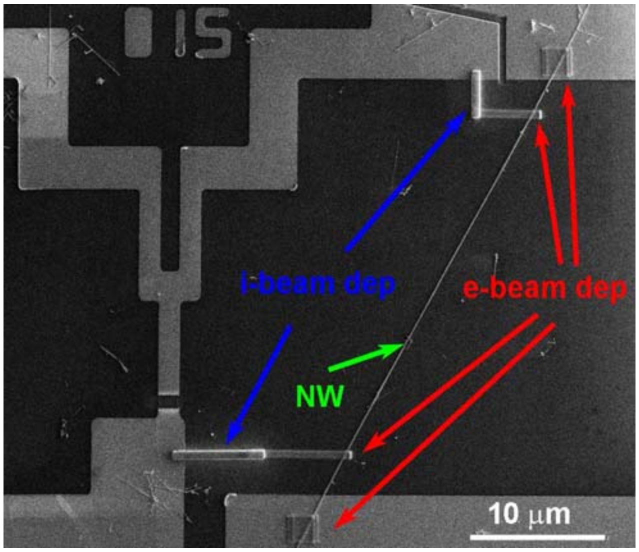

Figure 1: SEM image of a NW contacted using the standard procedure. Contacts made by focused electron- and by ion-induced deposition are indicated.

For gas sensing applications, this sample is introduced in a gas testing chamber and heated to a temperature above 200ºC, where the device operates as gas sensor. Furthermore, this temperature reduces the contact resistance and the device behaves as a resistor. The resistance of the NW is the magnitude that changes in the presence of the different gas atmospheres due to the adsorption of the oxidizing or educing gas species. The observed increase of the response towards gases with diminishing NW radius is a consequence of the increasing surface-to-volume ratio, valid for all gases measured. It is noteworthy to indicate that, for the case of CO, the detection level is below 5ppm, well below the legal limit for 8h exposure, which is 25ppm.

Finally, the long-term stability of these devices is reasonable, of few months, taking into account that it is a prototype.

3.2 Dielectrophoretic alignment of NWs

The problem of low throughput of the fabrication of gas sensing devices can be partially circumvented if it would be possible to correctly position the NWs on predetermined positions of the sample and, more concretely, bridging two contacts. In this way it would only be required to fix the NW to the contact, which is a much less time-consuming process. This can be achieved by DEP experiments, performed by driving an AC voltage between two electrodes while putting a drop of a solution containing the NWs [4]. In our case, the solvent is ethanol, which dries in reasonable short times to make this fabrication proves suitable for mass production.

When applying the AC voltage, for anisotropic objects, like NWs, its induced dipole moment interacts with the strong applied electric field. This forces the NWs to displace along the electric field gradient towards the region with the highest electric field, with which it lines up. The ad-hoc designed geometry of the electrodes used for DEP alignment is thought to have multiple confronted tips, as shown in figure 2. The upper inset shows one of these contact pairs bridged by one of the NWs. To extract the alignment yield after the DEP experiment, SEM observation has been used to count the number of NWs aligned between tips over the whole substrate. It is observed that the yield is maximum at low frequencies.

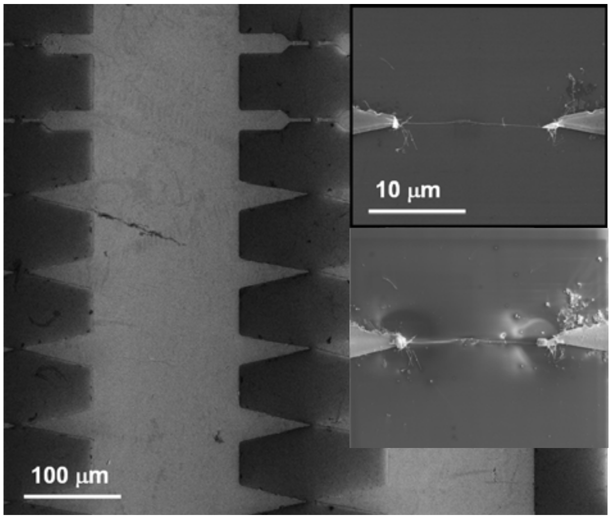

Figure 2: SEM image of the designed microelectrodes used to perform DEP experiments. The upper inset shows a NW aligned between 2 of the electrodes and the lower inset, the same NW after being fixed using electron assisted Pt deposition in the FIB.

Next, the bridging NWs are fixed to the contacts to ensure a good electrical contact. This is achieved by FEBID deposition on the two ends of the NW, as shown in the lower inset of figure 2. This procedure strongly reduces the deposition time inside the FIB machine and allows test and extract the electrical parameters of different devices in a very easy manner.

Figure 3 shows the operation of one of these devices as gas sensor towards different concentrations of CO. The CO pulses can be easily identified in the image, as well as the resistance drop in the presence of the reducing gas. This proves the feasibility of this approach.

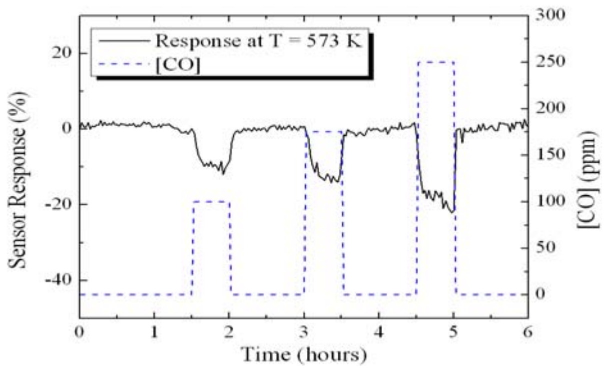

Figure 3: Response of the individual NW of figure 1 toward different concentrations of CO at 300ºC.

3.3 Microhotplates as substrates

One issue which appears when developing single NW-based sensing devices is the fact that to perform measurements it is required that the sample is heated to the above indicated temperatures. This is achieved, generally, by heating the complete measuring chamber, with a typical power consumption of several Watt. A way to circumvent this is the use of suspended MHPs as substrates for the NWs. These MHPs are clearly shown in the SEM image of figure 4. If the NWs are positioned on top of the MHPs and contacted to the patterned electrodes, the two terminal device will look like those in figures 1 and 2. This has been achieved in the same way as on standard substrates, using ethyleneglycol as solvent. The Pt nanostripes are fabricated using exclusively FEBID, because in these MHPs the distance between two pairs of interdigitated electrodes is quite reduced and, thus, the resistivity ot the Pt nanostripes does not play a major role.

For the operation of this MHP with individual NWs as gas sensor device, it is only necessary to heat up the suspended MHP, keeping the rest of the sample at or close to room temperature. And this can be achieved with the integrated heater which is fabricated at the bottom surface of the MHP. Figure 5 shows the power consumption for several of these MHPs, and it can be seen that 15mW are enough to heat the NW to 600K. Additionally, and this is a natural consequence of nanotechnology, the heating and cooling characteristic times can be reduced to few milliseconds, making the device extremely fast. This allows opens the possibility to operate the sensor in pulsed mode, heating it only for a short time and with arbitrarily long periods without heating.

The gas sensing response of devices fabricated on top of suspended MHPs is shown in figure 6 for two different temperatures achieved at two different power supplies. The resistance change for the highest temperature, 450K, has been obtained with a power supply of only 7.5mW

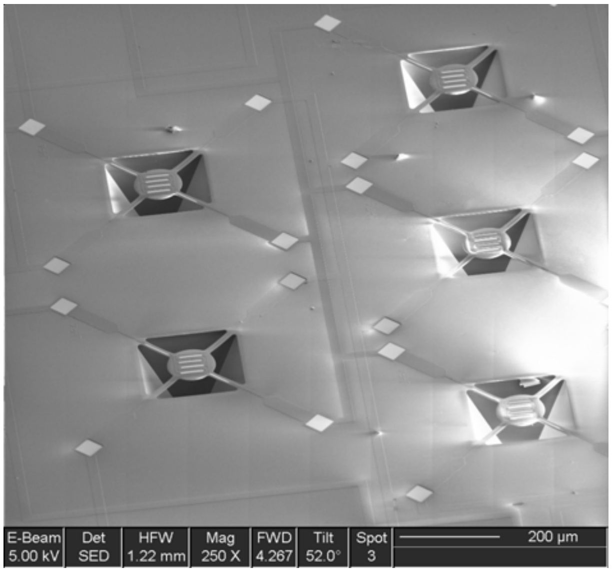

Figure 4: SEM image showing a group of 5 suspended MHPs on a single chip.

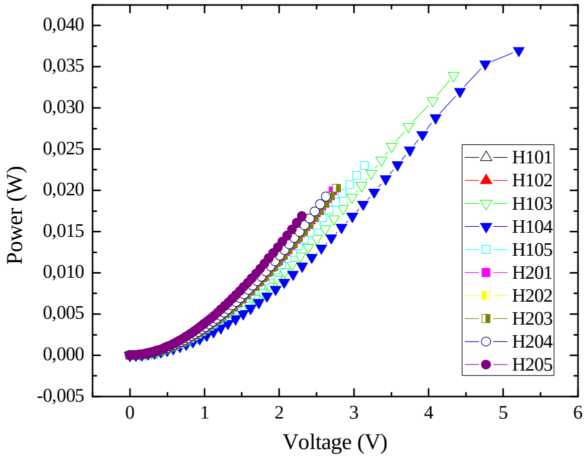

Figure 5: Power vs voltage characteristics of the MHPs of figure 4. The temperature of 600K is achieved at a supplied power of 15 mW.

4 CONCLUSIONS

In this work the fabrication process of gas nanosensors based on individual metal oxide nanowires has been presented, making use of the possibilities of focused ion beam technology. The prototypes fabricated with this methodology have been extensively tested and are operative towards different gases.

With the aim of reducing fabrication complexity, time and cost, alternatives to the fabrication have been presented. One is based on the use of dielectrophoresis for the manipulation and alignment of the nanowires between pairs of contacts, bridging them, reducing the amount of time of focused ion beam required to fix them to the contacts. A second alternative consists in the integration of the nanowires into suspended microhotplates, containing interdigitated electrodres and integrated heaters. The use of microheaters enables fast and reproducible modulation of the temperature with low power consumption, confirming them as possible components of future portable nanodevices.

In both cases, the fabricated devices show electrical and gas response characteristics similar to those fabricated on microelectronic substrates.

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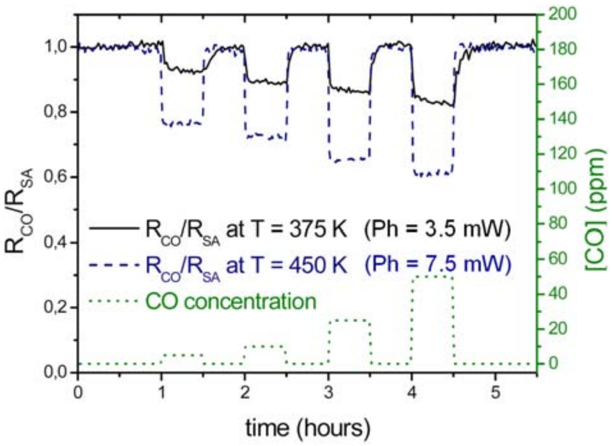

Figure 6: Responses of an individual NW, contacted on top of a MHP, towards varying concentrations of CO and different temperature, achieved with extremely low power consumptions.

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