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Functionalized ZnO microbelt as improved CO sensor

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Abstract

Miniaturized gas sensors are increasingly important to monitor the quality of air in a wide range of human environments. Semiconductor metal oxides have proved to be a useful family of materials, in this direction. Unfortunately, metal oxide sensors need a high temperature to respond to any target gas. In order to work around this limit, we fabricate hybrid sensors consisting in single zinc oxide microbelts decorated with organic molecules. Fluorinated tetraphenylporphyrin (H_2TTPF) is deposited via supersonic molecular beam and considerably improve the performance of the microsensor. The microdevice is investigated with XRD, SEM and AFM techniques. While the as-is ZnO microbelt shows no response up to 150°C, the H_2TTPF decorated microsensor shows a clear and quick response even at 75°C.

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Keywords:gas sensor; zinc oxide; carbon monoxide; hybrid; tetraphenylporphyrin

1. Main text

Detection of minor gas leaks is becoming one of the most important challenges today, in order to have clean and safe ambient for humans to live and work in. The last decades saw a continuous increase of new approaches to gas sensing: new materials, new architectures, new fabrication techniques, new data analysis and so on. Semiconducting metal oxides (MOs) have always been among the most attractive materials, and were strongly investigated as gas sensors. Among them SnO_2 and ZnO were the most studied for the detection of a wide variety of gases. When a

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metal oxide is exposed to certain gas, a resistance change is usually produced. After thick films and thin films, recently micro- and even nanostructures are being used, with a large improvement of performance and possibility to monitor the environment more extensively [1].

Unfortunately, metal oxide-based gas sensors work at relatively high operating temperatures, typically several hundred degrees (200-500°C) in order to obtain an optimum sensor performance [2-5]. Such high temperatures are not always possible, and the emerging demand on low power consumption is leading to lower operating temperature. For this reason, our approach consists in a single ZnO microbelt contacted on both sides with silver-paste drops.

Such architecture is then decorated depositing a very thin layer of organic molecules (fluorinated tetraphenylporphyrin) via supersonic molecular beam deposition (SuMBD). The H_2TTPF decorated microbelt is then used as a conductometric gas sensor for the detection of carbon monoxide.

2. Experimental

2.1. ZnO microbelts growth

The zinc oxide microbelts were synthesized by a solid-vapor process. Three grams of ZnO powder were loaded in an alumina boat, then positioned in the middle of an alumina tube. An Al_2O_3pad was used as substrate, which was placed downstream from the ZnO source powder at 20 cm to the end of the tube.

The tube was then inserted in a horizontal tube furnace, in which the source material was situated at the highest temperature. The deposition chamber was pumped down to around 2.5 Pascal overnight to evacuate residual oxygen and water vapor. Then the source powder was heated to 1475°C. Argon carrier gas was introduced at a flow rate of 50 sccm (standard cubic centimeters per minute) once the temperature reached 300°C.

The source was heated at 1475°C for 60 min. The ZnO microbelts were deposited onto the alumina substrate, which was placed at a temperature of 500-600°C under a pressure of 1000 Pascal. Then the furnace was turned off, and the tube was naturally cooled down to room temperature under argon flow.

2.2. Microsensor fabrication

The alumina substrate covered with ZnO microbelts was gently scratched on top of a thin (125 microns) kapton substrate. Subsequently, a single zinc oxide microbelt was selected and positioned manually under an optical microscope. Once it was in the appropriate position, two silver-paste drops were used to contact the two extremities. Thus, the microbelt becomes a single-crystalline bridge that can be used as a conductometric gas sensor.

2.3. Organic decoration via SuMBD

The microbelt functionalization was carried out via supersonic molecular beam deposition. A detailed description of the technique and the apparatus is given elsewhere [6,7]. Basically, H_2TPPF was seeded in a supersonic beam of He, reaching a kinetic energy of ~7eV and impinging the substrate in a chamber at a base pressure of $1 \cdot 10^{-7}$ mbar.

The typical organic arrival rate on the substrate was about 0.1nm/min, as evaluated from a quartz microbalance, and has been kept constant during all experiments. The microbelt was deposited a layer of fluorinated tetraphenylporphyrin molecules (99.9%, Sigma Aldrich) with a nominal thickness of about 26 nm.

2.4. Sensor measurement

Gas sensing properties of the microsensor were studied in a home-built apparatus including a test chamber, a sensor holder which can be heated up to 500°C, some mass flow controllers connected to high purity gas bottles, a multimeter (Keithley 2700), an electrometer (Keithely 6487A), and a home-built data acquisition system (Agilent, WEE Pro). The sensing measurements were run with an operating voltage of 1 V between the electrodes. We used the definition of response as the ratio between the resistance of the device during the gas injection and its resistance

in air. Response and recovery times are defined as the time to reach 90% of the complete response and to recovery 90% of it.

3. Results and discussions

3.1. Materials characterization

Morphology of the microbelt is shown in Fig. 1 (a), where a single zinc oxide microbelt is bridging two silver paste drops. The SEM image illustrates a single-crystalline microbelt whose uncovered part is 220 microns long. The belt width is around 5 microns, while its height seems to be about two microns.

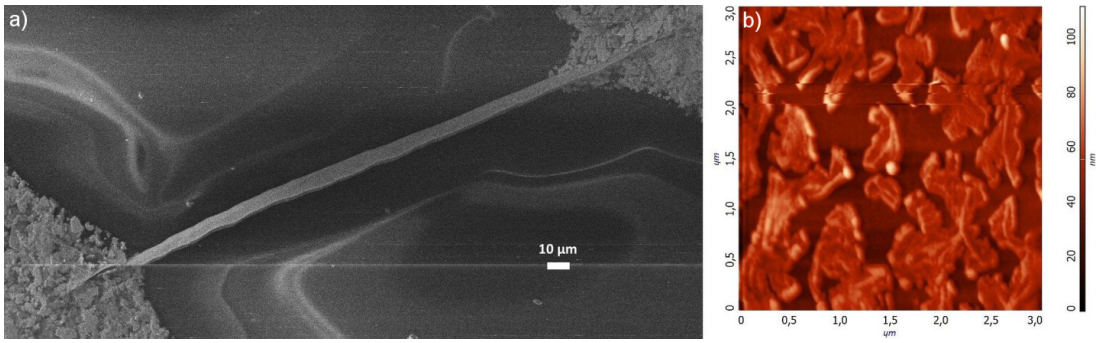


Fig. 1. (a) SEM image of a whole microdevice before functionalization. (b) AFM image (scan area is 3x3 micron^2) of the functionalized surface of the microbelt. The H_2TPPF islands are clearly visible.

Figure 1 (b) shows a detail of the ZnO microbelt once functionalized with the organic layer of H_2TPPF molecules. As can be seen in Figure 1 (b), the fluorinated tetraphenylporphyrin molecules do not form a smooth layer, but aggregate in fractal islands whose height is few tens of nanometers and areas range around 0.5 µm^2.

3.2. Sensing performance

The sensors resistance was tested from -1 V to +1V, finding a very good ohmic behavior of the device. The pure ZnO microbelt resistance was found 353 kΩ at 75°C and decreasing at 285 kΩ at 100°C. The functionalized microbelt showed a resistance of 600 kΩ at 50°C decreasing at 310 kΩ at 75°C down to 212 kΩ at 100°C.

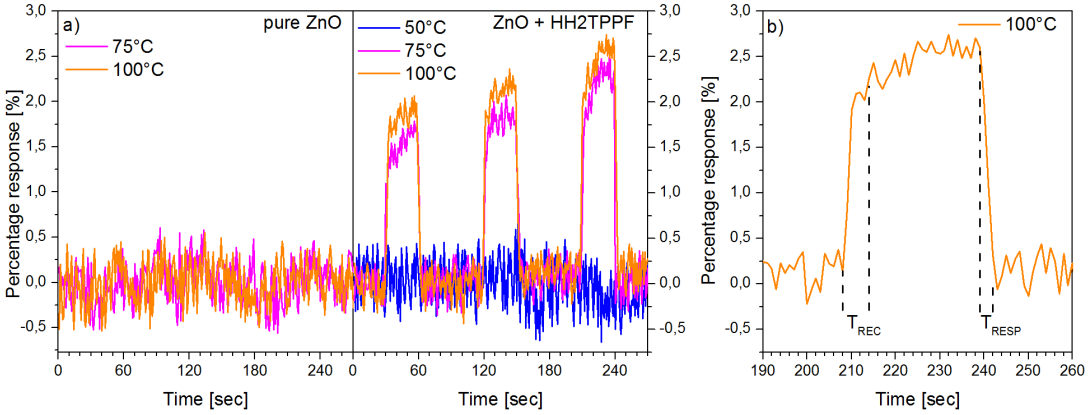
The usual working temperature of ZnO sensors is 300-500°C, and CO is a reducing gas for it, releasing electrons when gas molecules adsorb on the surface. Therefore, pure ZnO at high temperature is expected to undergo a decrease of resistance upon injection of carbon monoxide.

As can be seen in the left pane of Fig. 2 (a), pure ZnO microbelt does not respond at all at any concentration of CO gas (10, 25 and 50 ppm), both at 75 or 100°C. On the other hand, a prompt and clear response is visible in the right panel of Fig. 2 (a) for the H_2TPPF-ZnO sensor when carbon monoxide is injected in the chamber. The response of the hybrid microsensor is maximum at 100°C, a bit lower at 75°C, and disappears at 50°C.

The organic layer effect on the microdevice is not only a decrease of the operating temperature, but also a change in the sensing mechanism of the system as a whole: the resistance of the decorated belt increases when the CO gas in injected, and decreases when it is evacuated from the chamber.

This means that the sensing mechanism happens at the organic level, and is then transferred at the metal oxide structures that acts as a transducer.

Based on the sensitivity at low gas concentration and using the default definition of 3 standard deviation of noise, we calculated a limit of detection of 1 ppm at 75°C and 500 ppb at 100°C.



A zoom of a response peak is shown in Figure 2 (b), that makes clear how both response and recovery times are very quick, in the range of few seconds. This is valid for all working temperatures and all gas concentrations, as can be seen in Figure 2 (a), right panel.

Fig. 2. (a) Left panel: response of pure ZnO microbelt at different CO concentrations. Right panel: response of the hybrid system at 10, 25 and 50ppm of CO gas, at different working temperature. (b) Zoom of a peak from Figure 2 (a) showing how the response and recovery times are calculated.

4. Conclusions

We have realized hybrid microsensors for the detection of low-concentration CO at low temperature. The decoration of the ZnO microstructure with an organic layer of fluorinated tetraphenylporphyrin affects the sensing mechanism and makes possible a clear and quick detection of low CO concentration at 75°C, while pure ZnO shows no response at all.

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