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Zinc oxide nanowire based hydrogen sensor on SOI CMOS platform

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Abstract

Here we report on the successful low-temperature growth of zinc oxide nanowires (ZnONWs) on silicon-on-insulator (SOI) CMOS micro-hotplates and their response, at different operating temperatures, to hydrogen in air. The SOI micro-hotplates were fabricated in a commercial CMOS foundry followed by a deep reactive ion etch (DRIE) in a MEMS foundry to form ultra-low power membranes. The micro-hotplates comprise *p+* silicon micro-heaters and interdigitated metal electrodes (measuring the change in resistance of the gas sensitive nanomaterial). The ZnONWs were grown as a post-CMOS process onto the hotplates using a CMOS friendly hydrothermal method. The ZnONWs showed a good response to 500 to 5000 ppm of hydrogen in air. We believe that the integration of ZnONWs with a MEMS platform results in a low power, low cost, hydrogen sensor that would be suitable for handheld battery-operated gas sensors.

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1. Introduction

There has been increasing demand of detecting toxic and inflammable gases for industrial, environmental and many other applications. These demands have led to the development of a range of different gas sensor technologies. However, these discrete gas sensors are expensive (average cost is €10)

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and consume high power (~200 mW). The high cost is due to the low volumes of production (hence made manually/semi-automated) and also the use of separate interface electronics using discrete components to monitor the sensor output. The semi-automated low volume production often makes their performance have poor reproducibility with perhaps 20% or more batch-to-batch variation. This has inspired our research group to develop gas sensors on a CMOS platform – because batch production in CMOS can give more reliable and reproducible sensors and also high volume production reduces per unit sensor device cost. In addition, the ability for on-chip integrated circuitry gives the sensor ‘value added’ features at no extra cost. However gas microsensors developed on CMOS can also benefit from gas-sensitive nanomaterials (because of their higher surface to volume ratio) to achieve higher sensitivity. But to grow nanomaterials often requires very high growth/anneal temperatures (500 to 850°C) and harsh chemicals that are not suitable for CMOS substrates. Here, we have developed a low temperature hydrothermal method to grow ZnONW on a micro-hotplate sensing area without damaging the CMOS substrate. The sensor device is essentially a low power thin membrane micro-hotplate with $p+$ silicon resistor (for heating) and top interdigitated metal electrode (for measuring sensing material resistance). ZnONWs show promising response in the presence of ppm levels of hydrogen and its lower cost and lower power consumption would be suitable for future handheld battery-operated gas sensors.

2. Micro-hotplate structure

The resistive gas microsensors incorporate both heater and sensing structures. It contains a $p+$ silicon micro-heater of diameter 150 μm and interdigitated electrodes to contact to the sensing materials. The electrodes were made from the top metal layer, which were exposed during the bond pad opening process steps. The micro-heater was isolated from rest of the chip by a thin oxide/nitride membrane of diameter 564 μm . The sensor was designed in Cadence (v5.0) and fabricated from a commercial foundry using a 1.0 μm SOI CMOS process. The membrane was formed at the wafer level by deep reactive ion etching (DRIE) from a second MEMS foundry, after the CMOS process was complete. Exposed aluminium electrodes form oxide when come in contact with air; hence, electroless (bump bonding) plating was carried out at the wafer level to deposit nickel/gold (Pac Tech, Germany) on top of the aluminium electrodes. A cross-sectional schematic of the device is shown in figure 1(a) and the top view of the fabricated device is shown in figure 1(b). The micro-hotplates were characterised at different parts of the wafer and also from wafer to wafer. A typical power vs temperature plot is shown in figure 2, from which it can be seen that it consumes only 23 mW to reach 300°C (with ZnONW coating on top). The structure

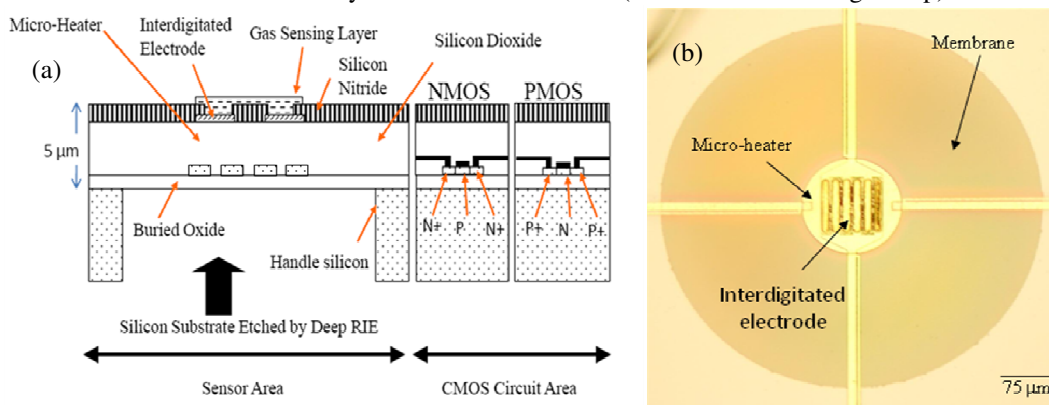


Fig1. (a) Cross-sectional view of CMOS micro-hotplate based gas sensor (drawing not to scale)
 (b) Optical microscope picture of top view of micro-hotplate and SOI membrane

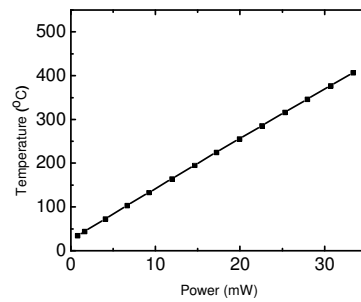


Fig2: Power consumption of an SOI CMOS micro-hotplate with ZnONW coating

of the micro-hotplate and its detailed analysis were reported in an earlier paper [1].

3. ZnONW growth on CMOS platform

Zinc oxide nanowires were grown on the membrane area using a CMOS friendly hydrothermal method. The thin (~5 nm) ZnO seed layer was sputtered on the micro-hotplates by using a shadow metal mask. This was then followed by dipping the chip in an equimolar (25 mM) aqueous solution of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma–Aldrich) and hexamethylenetetramine (HMTA, Sigma Aldrich) and was kept at 90°C for 2 h [2]. The devices were removed from the solution after the ZnONW growth and then washed with deionised (DI) water and dried with nitrogen. The scanning electron microscope (SEM) picture of ZnONW grown on our micro-hotplate is shown in figure 3.

4. Hydrogen test result and discussion

ZnONWs were tested in presence of hydrogen at the Microsensors and Bioelectronics Laboratory (MBL), University of Warwick, UK. The gas test chamber is computer controlled and there is facility to add dry and humid air along with the test gas to control the concentration. National Semiconductor DAQ card was connected to the chamber to capture the sensor data in a computer. The chamber was kept at 24°C. The sensor devices were heated up by silicon heaters which were under the ZnONW sensing layer. The test was carried out at six concentrations of hydrogen starting from 800 ppm to 4800 ppm. The response ($\Delta R/R$) was found to be *ca.* 9% (800 ppm) and 20% (4800 ppm) in hydrogen at 20% r.h., as shown in figure 4. The measurements were carried out at three different temperatures. It was found that the ZnONW response increases with increasing temperature, as shown in figure 5. The maximum temperature used here was 320°C to avoid any electro-migration in the aluminium under the Au/Ni

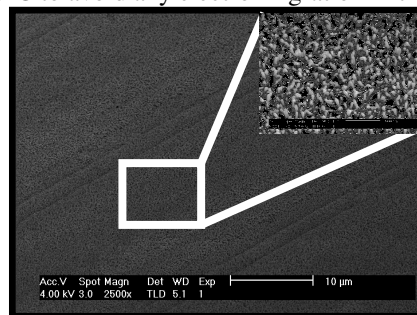


Fig3: SEM image of ZnONW grown on gold plated interdigitated aluminium electrode (inset shows magnified view)

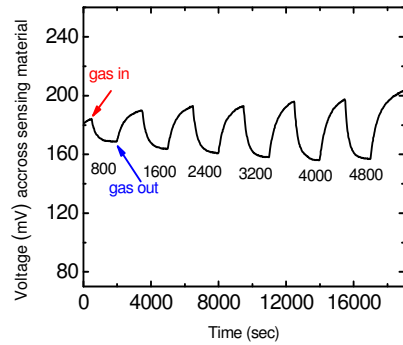


Fig4: Change in voltage across ZnONWs at different hydrogen concentrations at 320°C and r.h. of 20%.

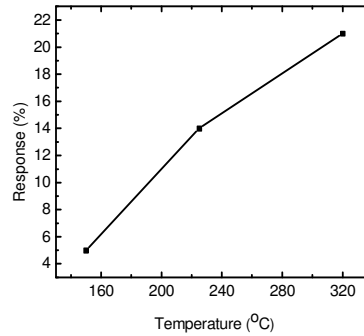
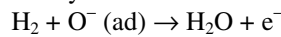
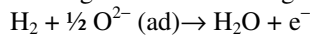


Fig5: Response ($\Delta R/R$) of ZnONWs to 4800 ppm of hydrogen at three different temperatures.

electrodes. It is well known that metal oxide gas sensitivity depends on the interaction between the gas species and adsorbed oxygen ions (O^- and O^{2-}) on the surface of the material. An electron depletion region is formed (which leads to the increase in the resistance of the metal oxides) when ZnONWs placed at the air atmosphere. This is due to the extraction of conduction band electrons by the adsorbed oxygen ions. When the ZnONWs are exposed to the hydrogen gas, it will react with adsorbed oxygen ions and produce water molecules (as shown below), while the released electrons will contribute to the current increase (hence resistance decrease) through the nanowire [3], in other words, a decrease in the width of the depletion region thus enhancing carrier (n-type) mobility in ZnO.



5. Conclusion

This paper describes a novel hydrothermal method to grow ZnONW on SOI CMOS membranes. The method is CMOS friendly because it does not require harsh chemicals and high process temperatures (e.g. compared to a CVD approach). The basic gas sensor device was an SOI micro-hotplate structure that contains a $p+$ silicon micro-heater and gold plated interdigitated electrodes. The micro-hotplates have very low power consumption (< 20 mW, below 250°C) and were fabricated at the wafer level in a commercial foundry. The devices showed a good response down to a few hundred ppm of hydrogen in moist air. We believe this ZnONW growth on fully processed CMOS substrate could potentially be used to manufacture a low-cost hydrogen microsensor.

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