CMOS Alcohol Sensor Employing ZnO Nanowire Sensing Films

S. Santra[1]*, S. Z. Ali[1], P. K. Guha[2], P. Hiralal[1], H. E. Unalan[1], S. H. Dalal[1], J. A. Covington[2], W.I. Milne[1], J. W. Gardner[2], F. Udrea[1]

[1]*Engineering Department, University of Cambridge, 9 J J Thomson Avenue, Cambridge CB3 0FA, UK*
[2]*School of Engineering, University of Warwick, Coventry CV4 7AL, UK*
**Corresponding author: email-Address: ss778@eng.cam.ac.uk, tel: + 44 1223 748311, fax: +44 1223 748348*

Abstract. This paper reports on the utilization of zinc oxide nanowires (ZnO NWs) on a silicon on insulator (SOI) CMOS micro-hotplate for use as an alcohol sensor. The device was designed in Cadence and fabricated in a 1.0 µm SOI CMOS process at XFAB (Germany). The basic resistive gas sensor comprises of a metal micro-heater (made of aluminum) embedded in an ultra-thin membrane. Gold plated aluminum electrodes, formed of the top metal, are used for contacting with the sensing material. This design allows high operating temperatures with low power consumption. The membrane was formed by using deep reactive ion etching. ZnO NWs were grown on SOI CMOS substrates by a simple and low-cost hydrothermal method. A few nanometer of ZnO seed layer was first sputtered on the chips, using a metal mask, and then the chips were dipped in a zinc nitrate hexahydrate and hexamethylenetramine solution at 90°C to grow ZnO NWs. The chemical sensitivity of the on-chip NWs were studied in the presence of ethanol (C_2H_5OH) vapour (with 10% relative humidity) at two different temperatures: 200 and 250°C (the corresponding power consumptions are only 18 and 22 mW). The concentrations of ethanol vapour were varied from 175 – 1484 ppm (pers per million) and the maximum response was observed 40% (change in resistance in %) at 786 ppm at 250°C. These preliminary measurements showed that the on-chip deposited ZnO NWs could be a promising material for a CMOS based ethanol sensor.

Keywords: Gas Sensor, SOI CMOS, Carbon nanotube, Zinc oxide nanowire
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INTRODUCTION

Semiconductor gas sensors based on metal oxides are widely used to detect toxic, inflammable gases and vapours and have been well documented in the literature [1 – 4]. They are low cost and can detect a large range of gases with high sensitivity and reasonable response times. The working principle of these semiconductor gas sensors is mainly based on the change in conductivity of the material upon exposure to a target gas. The use of a micro-heater to raise the temperature of the sensing material can induce better sensitivity and quicker response times.

In recent years, significant interest has emerged in the synthesis of one-dimensional nanomaterials because of their potential application in various fields [5–7]. The large surface to volume ratio and hence high surface area of these nanoscale materials make them attractive for gas sensing. Among different metal oxides nanowire (e.g. SnO_2, TiO_2, WO_3 etc.), zinc oxide (ZnO) is one of the most promising, with its wide band gap (3.37 eV at room temperature) and large exciton binding energy. ZnO nanowires are n-type semiconductors with high thermal stability and, on the contrary to most oxide nanowires, can be grown at low temperatures via a hydrothermal method. ZnO thin or thick films, which are either deposited or grown on non-CMOS substrates, have already been extensively studied for gas sensing applications. In particular, they were used to detect ethanol (1 – 5 ppm (pers per million)) [8, 9], NO_2 (0.5-8.5 (ppm)) [10], humidity in the range 12 – 96.9% [11], H_2 (600 ppm) [10, 13, 14], NH_3 (30 ppm) [12, 13]. The integration of ZnO nanowires, with a fully compatible CMOS technology, would be highly desirable as it enables 'smart' smaller sensors to be fabricated at a lower cost than conventional gas sensor manufacture. The combination is also additionally useful as the sensor can be combined with on-chip circuitry for signal conditioning and to compensate for some of the short comings of the sensing material, i.e. drift, non-linearity, aging etc.

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Here, we present a micro gas sensor based on ZnO NWs deposited onto CMOS micro-hotplates and evaluated its sensitivity to ethanol vapour in air.

MICRO-HOTPLATE FABRICATION AND ZNO DEPOSITION

The micro-hotplates were designed in Cadence (5.0) and fabricated at a commercial (XFAB, Germany) foundry using a 1.0 μm, three metal, polysilicon SOI process. The interconnect metal (aluminum) of the SOI process was used to form a micro-heater. The micro-heater itself is used as a temperature sensor because its resistance increases as a function of temperature.

Interdigitated electrodes (aspect ratio 56) were formed using the top metal electrodes, and the passivation above them removed using the same process step that is used to expose the bond pads of the chip. The micro-heater was then thermally isolated from the substrate by a Deep Reactive Ion Etching (DRIE) back etch at a commercial MEMS foundry (Silex Microsystem, Sweden) to reduce the power consumption. This resulted in an aluminum micro-heater embedded within a thin membrane (ca. 5μm) of silicon dioxide, with a passivation of silicon nitride. The cross-sectional view and the optical microscope picture of the fabricated device are shown in Fig. 1 and Fig. 2 respectively. The heater is of 75 μm radius with the corresponding membrane size of 280 μm.

Aluminum interdigitated electrodes tend to form an oxide when exposed to air, and therefore do not provide good electrical contact with the sensing material. Therefore electroless plating was carried out to deposit nickel followed by gold. The process was carried out at the wafer level to remove oxides from the exposed Al layer and electrolessly plate Ni/Au on only the exposed aluminum pads (Pac Tech (Germany)).

The micro-heaters were characterized on several devices across the wafer and it was found that 300°C can be reached with around 27 mW of DC power (as shown in Fig. 3).

For sensing material growth, a thin ZnO seed layer was sputter deposited (~5 nm) on selective areas of our CMOS devices using a metal mask. Following seed layer deposition, these devices were dipped in an equimolar (25 mM) aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and hexamethylenetramine (HMTA) and were kept at 90°C for two hours [15]. The devices were removed from the solution at the end of the growth, rinsed with DI water and dried under nitrogen flow. The chips were then annealed at 300°C for one hour. The advantage of this method is that ZnO NWs can be simultaneously grown on more than one micro-hotplate and hence can be extended as an inexpensive approach for wafer level fabrication.

The surface morphologies of the samples and size distribution of the nanowires were characterised using

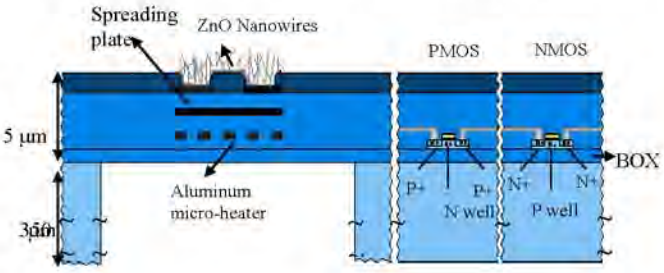

Fig. 1. Cross sectional view of the ultrathin (5 μm) SOI microhotplate and the CMOS electronic cells.

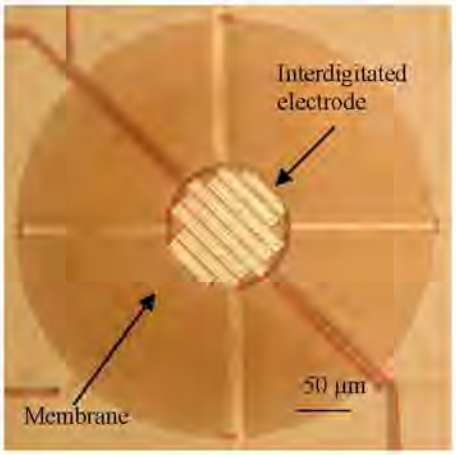

Fig. 2. An optical microscope picture of the fabricated micro-hotplate with interdigitated electrode.

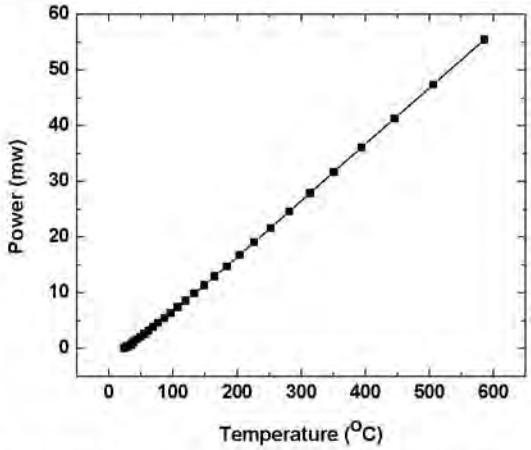

Fig. 3. Power vs temperature plot of the Al micro-heater.

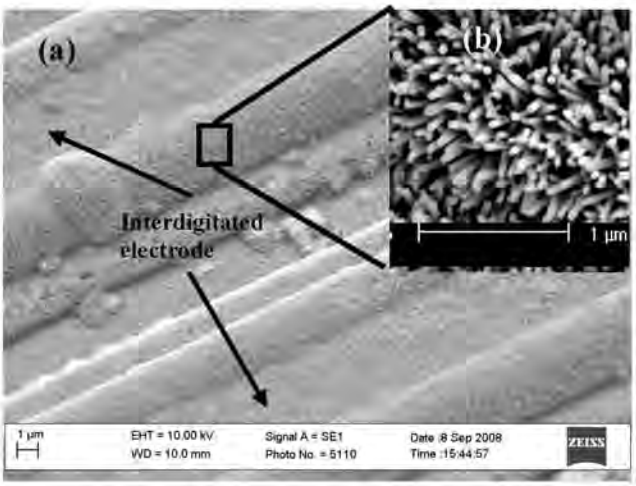

Fig. 4. (a) Top view of the SEM images of the ZnO NWs on interdigitated electrode, (b) zoom in view of NWs.

a field emission scanning electron microscope operated at 10 keV which is shown in Fig. 4. Nanowire length is ~400 nm and their diameter is ~60 – 80 nm. These nanowires are touching each other that provides the electrical paths between the pads of the electrode.

The current – voltage (I – V) characteristics of ZnO NWs was measured (shown in Fig. 5) in air. The linear I–V characteristic also confirms good ohmic contact between sensing material (ZnO NWs) and electrodes.

ETHANOL TEST RESULTS

Chemical testing was performed at the Sensor Research Laboratory (SRL), Warwick University. Here there are custom test facilties that can be used to expose sensors to specific vapour and water concentrations in clean air. Humidity was kept constant at 3000 ppm throughout.

The sensor was mounted on to a ceramic package (16 pin DIL, Spectrum Semiconductor, USA) and mounted in a stainless steel chamber kept at 30± 1°C within a Dri-bloc™ heater. The chamber was connected to a National Instruments DAQ card within a PC so that the data acquisition was recorded automatically using Labview software.

The sensors were heated locally by the aluminium micro-heater, which is just underneith the sensing material area. Sensors were kept at two different temperatures (200°C and 250±3°C). The power consumptions to maintain these temperature is only 18 and 22±0.3 mW. The preliminary measurements were carried out at five different concentrations of ethanol vapour in air.

The ZnO NWs response at different ethanol concentrations (175 – 1484 ppm) were measured, as shown in Fig. 6. We found that the response of NWs to ethanol vapour is significant and takes place within a few minutes. Following the removal of ethanol vapor from the system, recovery of the ZnO NWs was observed to take few tens of minutes before their resistance gets back to the base line value.

The response of the sensor is defined in this work as [((Rb-Ra)/Ra)×100%] where Ra is the baseline resistance of ZnO NWs in presence of humid air and Rb is the resistance in presence of ethanol and humid air. Based on this definition the measured responses were calculated with different concentrations. This is shown in Fig 7.

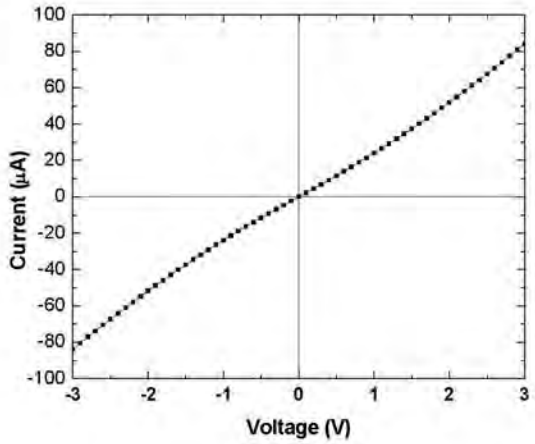

Fig. 5. I-V characteristics of ZnO NWs measured in air at room temperature.

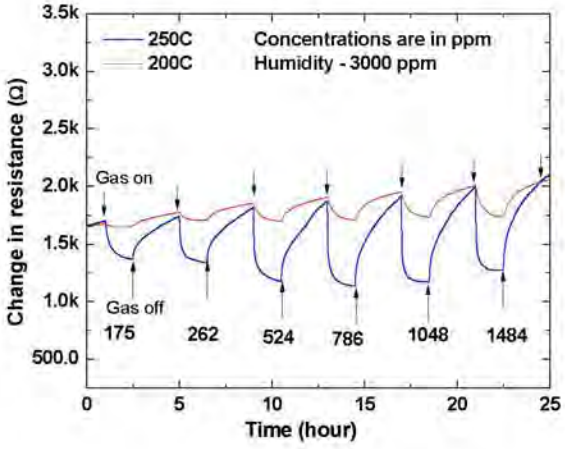

Fig.6. Change in resistance of the fabricated ZnO NWs ethanol gas sensor at different temperatures and different concentrations at a constant humidity of 3000 ppm.

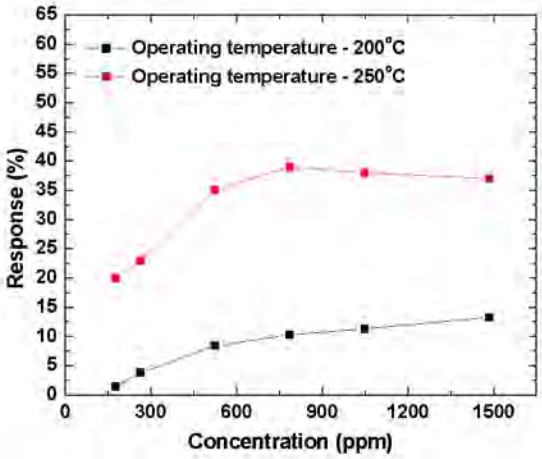

Fig.7. Response of the ZnO NWs measured as a function of ethanol concentrations.

DISCUSSIONS

It is well known that the sensing mechanism in case of most semiconducting oxide gas sensors is surface-controlled type [8, 9]. An oxygen molecule adsorbs on the surface of the ZnO NWs when it exposed to air. As a result an O–2 ion formed by capturing an electron from the conduction band. When these sensors are exposed to ethanol (reducing gas) at high temperature, the gas reacts with the surface oxygen species, which decreases the surface concentration of O–2 ion and increases the electron concentration. So the conductivity of the ZnO nanowires increases as can be seen in Fig 6.

In Fig. 7. we found that initially the fractional response increased with increasing ethanol concentration, but it flattens out at higher concentrations. More measurements are in progress to improve recovery time and explain the unexpected saturation effect.

CONCLUSIONS

This paper describes a method for the growth of ZnO NWs on SOI CMOS membranes. This method, as shown, is simple, economical, CMOS compatible and hence ideal for large scale wafer level production. The basic gas sensor device is a micro-hotplate structure containing an aluminium micro-heater embedded in a thin dielectric membrane, which allows us to achieve high temperatures with low power consumption. Following the growth of ZnO NWs, these sensors were exposed to different concentrations of ethanol vapor in air (RH 10%) and a maximum fractional response of 40% at 786 ppm was observed. These preliminary measurements show that on-chip ZnO NWs could potentially be used as a low-cost ethanol sensor.

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