Three technologies for a smart miniaturized gas-sensor: SOI CMOS, micromachining, and CNTs – challenges and performance

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Abstract

In this paper we propose a new type of solid-state gas sensor by combining three recent advances, namely silicon-on-insulator CMOS technology, through wafer etching and growth of gas-sensitive carbon nanotubes. We have developed novel tungsten-based CMOS micro-hotplates that offer ultra low power consumption (less than 10 mW at 250°C), on-chip CNT deposition at temperatures up to 700°C, and full integration of CMOS circuitry. Moreover, the tungsten micro-hotplates possess better stability than other CMOS materials such as polysilicon. The multi-walled CNT resistive gas sensors showed a good response to PPB levels of NO_2 in air but required additional heating to provide reasonable baseline recovery times. We believe that our approach is attractive for the mass production of low-cost, low-power gas sensors in silicon foundries.

Introduction

There is renewed scientific and commercial interest in solid-state gas sensors and in the related field of electronic noses because of recent advances in silicon microtechnology [1-5]. However, the problems of batch-to-batch reproducibility of gas-sensitive thick films and high power consumption have negated their use as accurate monitors of hazardous gases, whilst other sensor types (e.g. pellistor and electrochemical) are either too insensitive, power hungry or too expensive for the mass markets (e.g. automotive, PDAs, mobile phones). In wireless environment, DC power levels well below 100 mW (1 mW in pulse operation) are required at a suitably low cost. Recently reports on Carbon Nanotubes (CNTs) have created a lot of interest in gas sensing applications [6-10]. Carbon Nanotubes have unique electrical, mechanical and optical properties and, unlike bulk material, CNTs, have a high surface to volume ratio that results in good sensitivity even for small volumes. CNTs are sensitive to different toxic and VOC gases and the important aspect of the CNT sensor is that it could be operated at lower temperatures for detecting very low concentrations of NO_2 or other toxic gases as well.

We present here an ultra-low power smart gas-sensor with innovative CMOS micro-hot plate design and an integrated, fully compatible gas-sensitive CNT layer. We have achieved this through the challenging integration of three major technologies:

(i) High temperature thin SOI CMOS process using tungsten metallization: The use of CMOS offers full integration of drive, processing and read-out circuitry. Thin SOI offers additional electro-thermal isolation and the option of using the buried oxide as an etch stop during Deep Reactive Ion Etching (DRIE). The use of tungsten metallization allows junction temperatures up to 250^{o} C with no risk of electro-migration and negligible drift in time. Tungsten is used here both as an interconnect in the CMOS circuitry and as a layer for the micro-heater embedded in the microsensor.

(ii) Membrane technology using DRIE: The use of ultra-thin CMOS compatible membranes gives very low thermal losses and fast response times. Special attention was paid to back to front alignment, CMOS compatibility (removal of charge during DRIE de-clamping), suppressing over-etching effects and ensuring uniform etch across the wafer and from batch to batch.

(iii) CNT growth: High quality MW and SW CNTs were locally grown, self-aligned onto the pre-formed sensing metal electrodes. For this the embedded tungsten micro-heater was powered up to temperatures in excess of 700 ^{o}C. By optimizing the heater shape, it was possible to optimize the heat flow within the heater region and hence improve its temperature uniformity with variation of only 1%. Since the high temperature was confined to the heater region during the CNT growth the electronic circuitry was unaffected.

Micro-Hotplate Design

The device schematic cross-section and photographs of the manufactured smart sensors are shown in Figures 1-3. Two major designs have been employed. The first is based on silicon/tungsten resistive heaters and the second is based on a novel FET heater, the latter having the advantage of the temperature MOS gate control. All the layers used for the microheater, as well as the sensing electrodes, are formed during the CMOS sequence, with no additional post-processing steps required. A thermal sensor in the form of an SOI thermo-diode or a silicon resistive temperature detector (RTD) was integrated directly below the heater to monitor accurately the temperature during operation. The membrane was formed using a low

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frequency DRIE technique that ensured good uniformity and no under-notching effects. The membrane deflection was measured across the CMOS SOI wafers and from wafer to wafer both at room temperature and elevated temperatures (when the micro-heater was powered up). The deflection/diameter ratio was around 1% and the deflection increase with temperature was only 1nm/^{o}C (Fig. 4). These were indications of low residual and thermally-induced stress. The power consumption was below 15 mW at 250 ^{o}C for a 500 μm (diameter) membrane and below 8 mW for a 300 μm membrane.

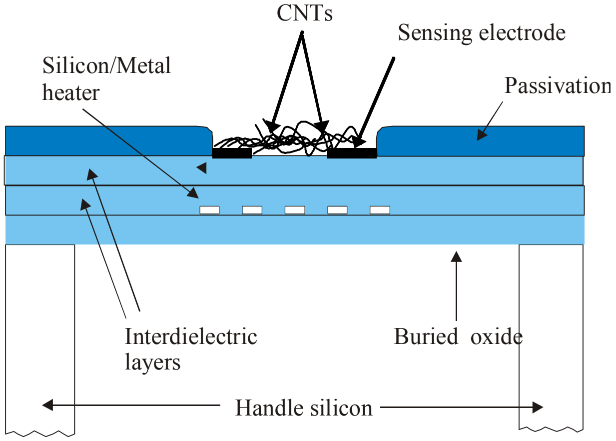

Fig. 1 Cross-section of resistive heater based resistive gas sensor with local growth of vertical CNTs above. CNTs can be Spaghetti like structures shown here.

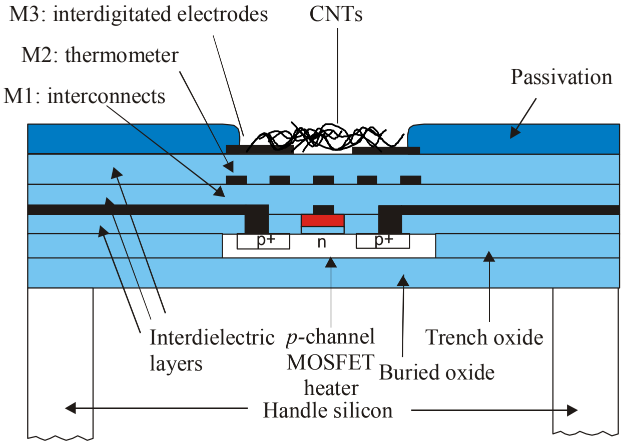

Fig. 2 Cross-section of FET heater based resistive gas sensor with integrated tungsten heater structure. CNTs are formed by local growth, above the third metal (which forms the detection electrodes)

CNT Growth

On-chip growth of carbon nanotubes [16] has been achieved by using the microhotplates as the thermal source for depositing CNTs locally on the interdigitated electrodes (IDEs). The SEMs of the locally grown multi-wall Carbon Nanotubes (MWCNTs) are shown in Figs. 5 and 6 with Raman spectroscopy depicted in Fig. 7.

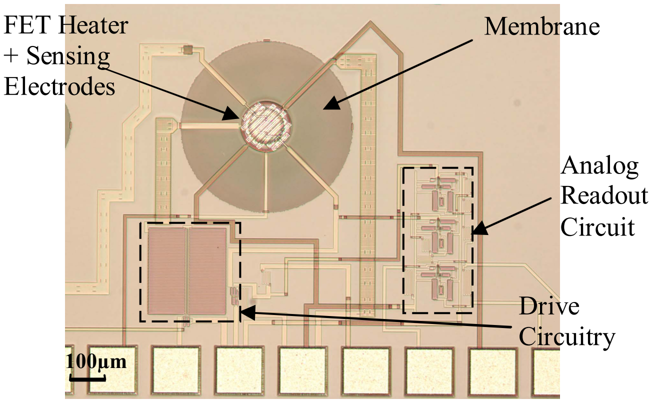

Fig. 3 Fabricated FET heater based micro-hotplate with integrated CMOS SOI electronics. Back-to-front alignment is within 1 μm which ensures high reproducibility chip to chip and batch to batch.

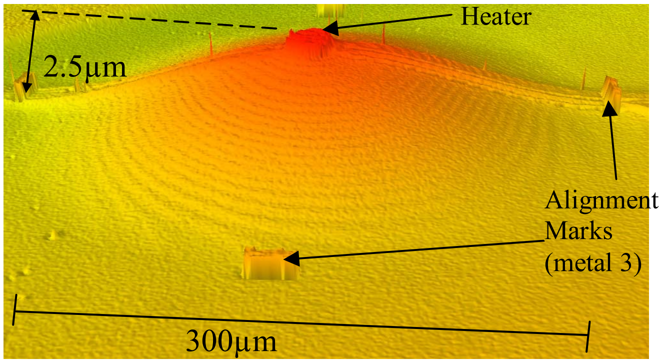

Fig. 4 Interferometer image showing the deflection (not to scale) of a fabricated microhotplate. The deflection is below 3 μm for a 300 μm diameter at room temperature. The deflection grows with a very low rate of ~ 1 nm/^{o}C at high temperatures. This is an indication of both low residual stress and low thermally induced stress in the layers.

The resistance of the sensing layer and the microhotplates were stable even after 600 hours of operation showing very good reliability of CNT based sensing devices. As expected, the high thermally conductive layer of CNTs has no impact on the power consumption, while bulk CNT growth can increase the power consumption quite significantly, e.g. by 20% (Fig. 8).

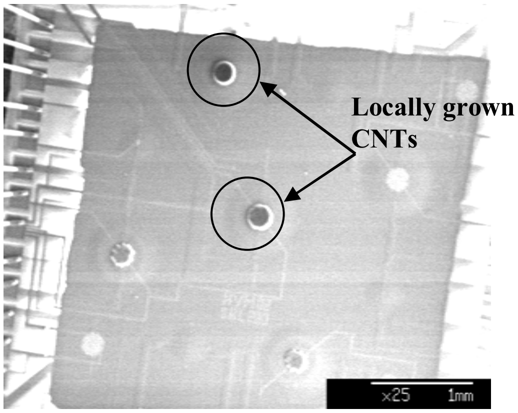

Fig.5 The SEM of a local growth on CMOS microhotplates using tungsten heater. Multi-chips were grown at the same time, by powering up the tungsten micro-heaters in parallel.

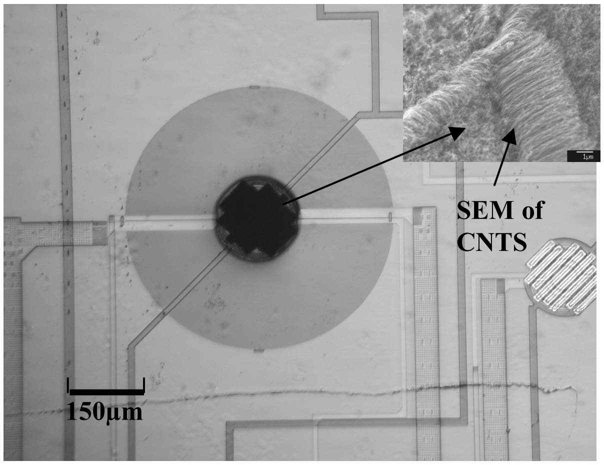

Fig. 6 Photograph of a CNT based gas sensor with the dark area showing the CNTs. The inset picture is a zoom of the SEM showing 'spaghetti -like' CNTs.

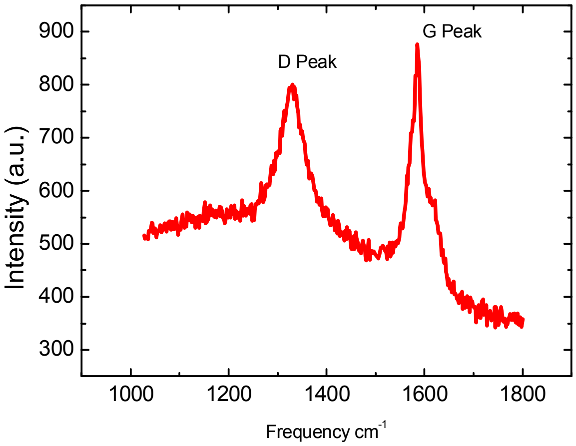

Fig. 7 Raman spectroscopy showing CNT formation on CMOS microhotplates.

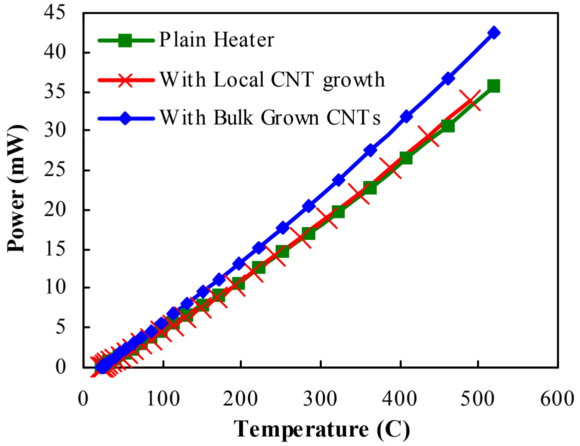

Fig. 8 The power consumption before and after CNT growth. The bulk growth has resulted in additional power losses due to high conductivity of the CNT layer. In contrast, local growth of CNTs did not impact the power consumption, as the sensing area is fully isolated from the rest of the chip though the membrane.

Results

The sensor was found to offer a response of 8 % to 100 ppb of NO_2 and 20% at 20 ppb before falling off at lower concentrations (Fig. 9). It showed improved recovery time of the zero gas line at elevated temperatures (few seconds). The best response was seen at room temperature but a higher temperature was required to refresh the baseline resistance. At higher temperatures the sensitivity is lower but no refreshing is required at an elevated temperature of 270°C (10 mA of heater current) for baseline recovery so there is slight trade off between sensitivity and reversibility. The thermal response time was in the order of few ms (Fig. 10) allowing fast thermal modulation of the micro-heater and pulse drive for further reduction of the power consumption. The CNTs were initially found to have poor stability, but after "conditioning", using the embedded micro-heater and drive beyond a certain stability point, the resistance of the CNT layer became stable if operated below 300 °C. The smart CNT micro-sensor also showed responses to methanol and ethanol (not shown here). The ultra-low power consumption of the hotplates and the growth of CNTs on multi-chips at the same time, in parallel, show great potential for high volume manufacturability.

The precise mechanism by which CNTs respond to oxidizing and reducing gases is not fully understood. Nevertheless it has been reported that it probably involves the sorption of oxygen molecules from the atmosphere onto the surface of the CNTS [6,8,14]. Then, for example, the gas reacts with the sorbed oxygen leading to the abstraction (or injection) of electrons into the conduction band of the carbon nanotubes.

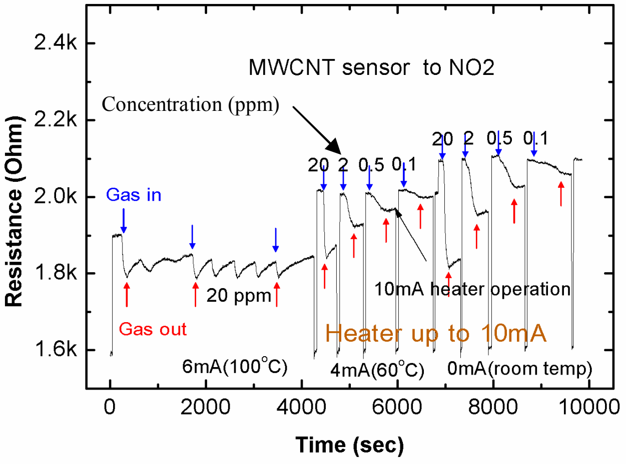

Fig. 9. Response of CNTs to 20, 2, 0.5, 0.1 ppm of NO_2. The response time was in the order of minutes, and the embedded micro-heater was used to speed up the recovery time (facilitate NO_2 desorption)

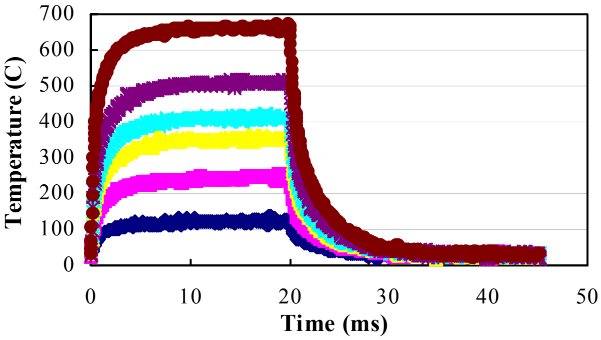

Fig. 10 Transient response of the heaters. Due to the very low thermal mass of the membrane, the thermal rise and fall times were very fast (few ms). This allows pulse drive for further reducing the power consumption.

It is believed that defects within the carbon nanotubes play an important role in their response to gaseous molecules because these defects create reactive sites and can be explained by theoretical investigations [11,12]. These defects can induce dangling bonds in the tube edges, ends and side-walls. It is also believed that the electrons are localized on the individual tubes and that the junctions between NTs can affect the mobility through the distance between CNTs varying [13,14]. At room temperature NO_2 molecule can dynamically co-exist with N_2O_4, NO_3 molecules which do not influence the density of states and have longer desorption time; therefore could be one of the reasons for the longer time recovery in the gas sensing process [15]. The baseline can be recovered quickly at high temperatures around 250° C – 300° C offering good stability of the CNT gas sensing devices at very low powers.

Conclusions

In this paper we have demonstrated a CNT based smart gas sensor. CMOS compatible micro-hotplates were fabricated followed by a fully compatible local growth of the CNT gas-sensing layer. A good sensitivity to NO_2 gas has been observed at room temperature and the embedded micro-heater was used to greatly improve the recovery time of the CNTs. The smart sensing device has ultra low power consumption, excellent reproducibility and good long-term stability, and we believe has strong potential as a commercial sensor.

Acknowledgements

The work was partly supported by the Ministry of Information and Communication, Republic of Korea, under project no. 2005-s-605-02 and by the Rural Development Administration, Republic of Korea, under project no. 20070501034006. F. Udrea, W. I. Milne and J.W. Gardner also acknowledge the award of the EPSRC project: EP/F004931 and the continuous support of the UK research council in this area.

References

(1) I. Simon, N. Barsan, M. Bauer, and U. Weimar, "Micromachined metal oxide gas sensors: Opportunities to improve sensor performance," Sensors and Actuators B, vol. 73, pp. 1–26, (2001)

(2) J. Suehle, R.Cavicchi, M.Gaitan, S. Semancik, "Tin oxide gas sensor fabricated using CMOS micro-hotplates and in-situ processing," IEEE Electron Device Letters, Vol 14 (3), pp.118-120, (1995)

(3) F. Udrea, J.W. Gardner, D. Setiadi, J.A. Covington, T. Dogaru, C.C. Lu, W.I. Milne, "Design and simulations of SOI CMOS micro-hotplate gas sensors," Sensors and Actuators B, Vol 78, pp. 180-190, (2001)

(4) M. Graf, D. Barrettino, K. Kirstein, and A. Hierlemann, "CMOS microhotplate sensor system for operating temperatures up to 500°C," Sensors and Actuators B, Vol 117, pp. 346-352, (2006)

(5) M. Afridi, J. Suehle, M. Zaghloul, D. Berning, A. Hefner, R. Cavacchi, S. Samancik, C. Montgomery, C. Taylor, "A monolithic CMOS Microhotplate based gas sensor system," IEEE Sensors Journal Vol2 No 6, pp 644-655, December (2002)

(6) J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, and H. Dai, "Nanotube molecular wires as chemical sensors" Science 287, 622 , (2000).

(7) S. Peng, K. Cho, "Chemical control of nanotube electronics", Nanotechnology 11, 57, (2000).

(8) P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, "Extreme oxygen sensitivity of electronic properties of carbon nanotubes", Science 287 (2000) 1801.

(9) M. Arab, F. Berger, F. Picaud, C. Ramseyer, J. Glory, M. Mayne-L'Hermite, "Direct growth of the multi-walled carbon nanotubes as a tool to detect ammonia at room temperature", Chemical Physics Letters, 433, 175 – 181, (2006).

(10) C. Cantalini, L. Valentini, I. Armento, L. Lozzi, J.M. Kenney, S.Santucci, "Sensitivity to NO_2 and cross-sensitivity analysis to NH_3, ethanol and humidity of carbon nanotubes thin film prepared by PECVD", Sensor Actuators B, 95, 195, (2003).

(11) J. Zhao, A. Buldum, J. Han, J.P. Lu, "Gas molecule adsorption in carbon nanotubes and nanotube bundles", Nanotechnology 13, 195 (2002).

(12) S. Santucci, S. Picozzi, F. Di Gregorio, L. Lozzi, C. Cantalini, L. Valentini, J.M. Kenny and B. Delley, "NO_2 and CO gas adsorption on carbon nanotubes: experiment and theory", Journal of Chemical Physics, Vol. 119, No. 20, pp. 10904-10910, (2003).

(13) L. Valentini, V. Bavastrello, E. Stura, I. Armentano, C. Nicolini, J.M. Kenny, "Sensors for inorganic vapor detection based on carbon nanotubes and poly(*o*-anisidine) nanocomposite material", Chem. Phys. Lett. 383, 617, (2004).

(14) L. Valentini, C. Cantalini, L. Lozzi, S. Picozzi, I. Armentano, J.M. Kenny, S. Santucci, "Effects of oxygen annealing on cross sensitivity of carbon nanotubes thin films for gas sensing applications ", Sensor. Actuators B 100, 33 (2004) .

(15) S. Peng, K. Cho, P. Qi, H. Dai, "An initial study of CNT NO_2 gas sensor ", Chemical Physics Letters 387, 271 – 276, (2004).

(16) M. S. Haque, S. Z. Ali, N. Rupensinghe, I. Haneef, P. Guha, F. Udrea, W. I. Milne, J. Park, S. Maeng, "Novel on chip growth of carbon nanotubes using high temperature microheaters", NT-07, 8th International Conference on the Science and application of Carbon Nanotubes, 24-29 June, p 15, A05, (2007).