

Nanotubes and Nanorods on CMOS Substrates for Gas Sensing

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Abstract. In this paper we discuss the combined use of integrated CMOS microhotplates employing nanomaterial sensing layers for intelligent, compact gas sensors with increased sensitivity, selectivity and fast response times. We first review the status of nanomaterial-based gas sensors, their operating principles, discussing growth issues and their compatibility with CMOS substrates. We then describe Multiwall (MW) Carbon Nanotubes (CNTs) and ZnO Nanowires (NW) growth/deposition onto CMOS microhotplates. The paper continues by discussing the response of these nanomaterial sensing layers to vapours and gasses. Finally we discuss the future prospects of nanomaterial-based CMOS gas sensors, highlighting on one hand their future potential and on the other hand their present shortcomings and future challenges that need to be addressed before they can be released commercially.

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

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INTRODUCTION

Gas sensors are widely employed for a variety of applications, such as environmental monitoring (toxic and inflammable gases), automobiles, process control (e.g. petrochemical and food industry), personal safety, medical and even military scenarios. Commercial gas sensors are based on electrochemical, catalytic, optical or solid state technologies. These sensors suffer from poor compatibility with CMOS (complementary metal oxide semiconductor) processes and their power consumption is significant (hundreds of mW to 1W). Modern solid state (resistive) gas sensors are generally based on wide-bandgap semiconducting metal oxide sensing materials. The development of these gas sensors has been extensively studied in the literature [1-4]. They have attracted the attention of scientists and industrialists due to: relatively low cost, robustness, simplicity of their use, large number of detectable gases, possible application fields etc. However, they do suffer from selectivity problems, as the sensing material tends to be sensitive to more than one gas. In addition, batch-to-batch reproducibility of gas-sensitive thick films and the high power consumption have impeded the use of such sensors as

accurate monitors of hazardous gases, while other sensor types (e.g. catalytic and electrochemical) are either too insensitive, power hungry or too expensive for mass markets.

In recent years, there has been increasing interest in integrating gas sensors with silicon CMOS technology. The aim is to increase the sensor's intelligence, reliability and ultimately reduce the physical dimensions of the system and its cost (by batch production). Nevertheless, the use of CMOS in sensors develops some constraints, e.g. any prolonged thermal treatment (which is often necessary for sensing material annealing) above 450°C of a CMOS substrate is not possible because of the low melting point of aluminium (Al, predominantly used in CMOS). In addition, most commercial gas sensor substrates use non-CMOS compatible materials to contact to the sensing film (such as Au or Pt). Hence the number of reported works [5-15] of CMOS gas sensors is still relatively small and there are few products available in the market. Last, but not least, CMOS is always marketed as a technology of low cost and high volume. In spite of its immense-potential, the gas sensor market is still considered today as being too small to justify the CMOS route.

As already mentioned, CMOS comes with the 'power' of miniaturisation. The small size means more portability and lower cost, but conventional metal oxides (in the form of bulk material) are no longer effective in micro gas sensors, as the lower surface area and causes lower sensitivity. As a consequence, over the past couple of years, there has been a shift in sensor research towards more sensitive gas sensing layers. Nanomaterials are strong candidates for analytical detection, because of their reduced dimensions that create structures with exceptionally high surface area. Thus there is a potential increase in sensitivity even for a miniaturized sensor area. Researchers have already demonstrated growth or deposition of different nanomaterials and their promising performance in gas detection [16-20]. Thus, it is immensely beneficial to combine the two technologies (CMOS and nano-sensing material) to achieve a 'smart' low power, low cost, small size, reliable and reproducible sensor product, making them ideal for use in portable or wireless applications. 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.

In this paper, we briefly discuss different nanomaterials used for gas sensor applications. We also review different processes for nanomaterials growth and discuss the challenges involved in integrating them with CMOS substrates. In the final part of the paper we review the work carried out at Cambridge and Warwick Universities, in the UK, to develop a CMOS gas sensor. Special emphasis is put on the design of CMOS micro-hotplates for low power and local growth of nanomaterials: carbon nanotubes (CNTs) and zinc oxide (ZnO) nanowires (NWs). Finally some gas testing results performed at Warwick University and ETRI (Korea) are included.

NANOMATERIAL GAS SENSOR

There have been reports of the use of different nanomaterials as gas sensing films. These materials show considerable resistance or temperature changes upon exposure to inorganic gases and volatile organics. Nanomaterials can be fabricated in the form of nanoparticles, nanoslabs, nanotubes, nanorods, nanowires etc.

Both multiwall (MW) and singlewall (SW) carbon nanotubes are strong contenders as nano gas sensing materials. Kong *et al.* [18] were among the first to demonstrate the response of Nanotube (NT) FET devices to NO₂ and NH₃ gases. After this initial report, in 2000, several groups [e.g. 21-24] have reported

different Carbon Nanotube (CNT) based chemical sensors. To date, researchers have already used CNTs to detect a variety of toxic gases including NH₃, NO₂, H₂, CH₄, CO, SO₂, H₂S and O₂ [25]. While CNTs show response to several gases, they seem to lack selectivity for a target gas. However, it is possible to increase the sensitivity and selectivity towards a particular gas by functionalizing the CNTs [e.g. 26-30]. This functionalisation can be done by metal and metal oxide decoration, polymer coating or atomic doping etc.

Another set of materials which have been widely studied in the literature are metal oxides. They are popular because of their better stability and their superior sensitivity towards a variety of gases. This is in contrast to CNTs that seem difficult to reproduce and often their drift in time and temperature is unacceptable. One idea that has been put forward is to create nano metal oxides taking advantage of both the nano geometry (with high surface area) while maintaining the stable sensing properties of metal oxides. Some of the materials already reported in literature for use as gas sensors are: Doped/ undoped ZnO nanowires, nanorods [31-35], tin oxide nanowires, nanoslab [36-39], titanium oxide nanoparticles, nanowires [20, 40], indium oxide [41, 42] and tungsten oxide nanoparticles [43].

However, all the above mentioned work is not on CMOS substrates. This is predominantly because of the constraints imposed by the CMOS process. In particular CMOS substrates are more sensitive to harsh environments (both thermal and chemical) that are often required for the synthesis and annealing of nanomaterials.

NANOTUBE AND NANOWIRE GROWTH OR DEPOSITION

There are many conventional ways to grow or deposit nanomaterials, however few are suitable for use on CMOS substrates. Two popular techniques are to grow nanomaterials by thermal or plasma enhanced (PE) chemical vapour deposition (CVD) and hydrothermal methods. Thermal CVD growth requires the substrates to be heated to a very high temperature (generally more than 500°C-depending on the specific recipe) which can be too high for the on-chip circuitry and internal metal layers. In PECVD the use of plasma can significantly damage the fragile micro electrical mechanical system (MEMS) structures. In addition, both the CVD methods are quite expensive. On the other hand, hydrothermal growth is simple, low cost and most importantly CMOS friendly. Though care needs to be taken to ensure that the chemicals used do

not affect the passivation layers on chip. Apart from the above two methods, researchers have also been using commercially available nanomaterials to deposit onto the devices by different techniques such as drop coating, dip coating, inkjet printing, spray coating, spin coating etc.; so that they can avoid the potential harsh environments necessary for nanomaterial growth. Even though these methods are low cost and CMOS friendly, the dispersion is difficult due to strong Van der Waals force. Thus, deposition of agglomerated bunches of nanostructures is inevitable and this leads to the poor sensitivity and slow response. Also these methods have their own problems, e.g. in inkjet printing one needs to use a very dilute solution to avoid any nozzle clogging or in case of dip coating one needs to cover bond pads to avoid any chemical contaminations. It is also necessary to mention that some of the above methods (except inkjet printing and drop coating) require conventional lithography approach (i.e. steps like deposition of photoresist, exposure of ultra violet light, lift off etc.) or use of some masking process (e.g. shadow mask) to grow/deposit nanomaterials on predefined areas of the chip. Furthermore, the use of these techniques is strictly speaking restricted to low volumes and hence negates the use of CMOS technology.

Here we will discuss three methods of growing nanowires and nanotubes on a fully processed CMOS substrate. To start with, we will briefly describe the Cambridge-Warwick CMOS chemical sensors.

The starting device is a micro-hotplate structure – a resistive metal heater thermally isolated from the substrate by a membrane formed by a back-side etch. Such micro-hotplate structures are used in micro-gas sensors to provide a high temperature during operation for better sensitivity and faster chemical response time.

Our devices have been fabricated using a commercial SOI (silicon on insulator) CMOS process to form the heater as well as the interdigitated gas sensing electrodes using the top metal layer – that is exposed using the same process step that is used to etch the passivation layer above the bond pads. The electrodes are used to measure the resistance of the gas sensing material that is grown/deposited onto the device. The CMOS process step is followed by a back-side Deep Reactive Ion Etching (DRIE) step to form the membrane. Several devices have been fabricated – some with aluminium metallization, and others with tungsten (W). The tungsten metallization was used in the process to sustain high temperatures as conventional CMOS metal (Al) cannot achieve temperatures in excess of 300°C reliably.

The basic structure of the chemical sensor is shown in Fig. 1. The optical microscope picture of the fabricated device is shown in Fig. 2. SOI is

particularly effective in this process, as the buried oxide acts as an etch stop during membrane formation. The membranes are very thin (~5 µm) yet very robust. The microhotplates using such thin membranes formed by CMOS dielectric layers are particularly power efficient. At 600°C the power consumption is merely 45 mW for a membrane diameter of 500 µm and a heater diameter of 150 µm. The thermal mass of the membranes is very small and hence they have very fast transient time (10 ms to 600°C), which enables pulse mode operation, further reducing the power consumption. The details of the micro-heater design and characterisation were reported in [44]. The power versus temperature plots of the tungsten and aluminum micro-heaters is shown in Fig. 3 (without sensing film).

We were successfully able to grow/deposit ZnO nanowires and CNTs on our CMOS substrates. We give here, as examples, two different methods to grow/deposit ZnO nanowires, and one method to grow MWCNTs.

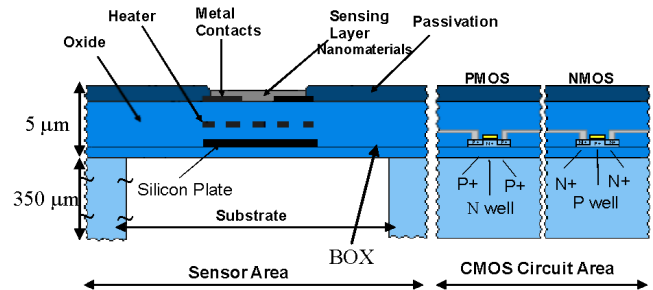


Fig. 1. Cross sectional view of the ultrathin (5 µm) SOI micro-hotplate and the CMOS electronic cells.

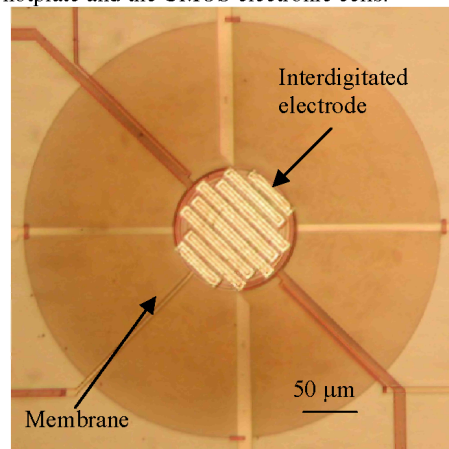


Fig. 2. An optical microscope picture of the fabricated micro-hotplate with interdigitated electrode.

(i) We have used hydrothermal methods to grow ZnO NWs on our above mentioned CMOS sensor device. For ZnO NWs growth, a thin ZnO seed layer was sputtered (~5 nm) on selective areas of our CMOS devices using a metal (shadow) mask. This was followed by dipping in an equimolar (25 mM) aqueous solution of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMTA) at 90°C for two hours [45]. The devices were removed from the solution at the end of the growth, rinsed with de-ionised water and dried under nitrogen flow. The chips were then annealed at 300°C for one hour. The surface morphologies of the samples and size distribution of the nanowires were characterised using a field emission scanning electron microscope operated at 10 keV, as shown in Fig. 4. Typical Nanowire length was ~400 nm and their diameter was ~ 60 – 80 nm. These nanowires are touching each other and hence provide electrical paths between the pads of the interdigitated electrodes.

This deposition method is simple, relatively low cost and most importantly CMOS compatible (although in large volume the cost of it cannot be neglected compared to other costs). Nevertheless, ZnO NWs can be simultaneously grown on more than one micro-hotplate and hence this method can be extended to wafer level fabrication.

(ii) We also reported on the growth of ZnO NWs without using a ZnO seed layer [46]. Here conventional lithography was used to deposit on-chip NWs in predefined areas, although deposited NWs are non-uniform because of the absence of seed layer. The SEM picture is shown in Fig. 5.

(iii) Here we have taken a novel approach of growing CNTs on standard CMOS substrates. The technique is known as ‘local growth’ [47, 48], where, instead of heating the whole chip/wafer, local heating (using the tungsten micro-heaters) is used to grow CNTs on-chip (i.e. in-situ) over a single micro-heater region. This method allows unique control over the position (self aligned to the hotplate region) and time of growth.

For (iii) CNT growth, firstly the chips were covered (except the bond pads of the chips which were masked to avoid shorting them) with a 2 – 4 nm layer of iron (Fe) catalyst using sputtering. Then the devices were mounted onto a ceramic package and connected within a printed circuit board to a power supply. The chips were then transferred to a CVD chamber to grow the CNTs. The chamber was pumped down to 0.2 mbar using a rotary pump. The micro-heater was powered through a computer controlled external power supply so that the centre of the membrane (the hotspot) can reach a high temperature e.g. 700°C. When the temperature over the micro-heater region was 400°C,

high purity ammonia (150 sccm) was introduced in the chamber using a mass flow controller (MFC). The micro-heater was kept at 725°C for 30 sec to form the small catalyst Fe islands. Then acetylene (75 sccm) was introduced through the separate MFC. The partial pressure was 4 mbar during growth process. The deposition time was typically 10 minutes, after which the gases were turned off and the devices were allowed to cool. It was found that the use of much higher temperatures (> 800°C) can give better quality CNTs, but can result in a rupture of the membrane. The nanotubes are formed due to the decomposition of acetylene, from which carbon dissolves and diffuses through the catalyst. The CNTs formed in this way are spaghetti like (and multiwall), but are useful for gas sensing applications and offer better conducting paths than vertically aligned nanotubes. The optical microscope picture of the gas sensor devices with MWCNTs and SEM pictures are shown in Fig. 6 and 7.

GAS SENSING PRINCIPLE

It is well known that the sensing mechanism in case of most semiconducting oxide gas sensors is a surface-controlled effect [17, 31]. An oxygen molecule adsorbs onto the surface of the metal oxide NWs when it is exposed to air. As a result an O_2^- ion forms by capturing an electron from the conduction band. When these sensors are exposed to reducing gas at high temperature, the gas reacts with the surface oxygen species, which decreases the surface concentration of O_2^- ion and hence increases the electron concentration, meaning the conductivity of the metal oxide nanowires increases.

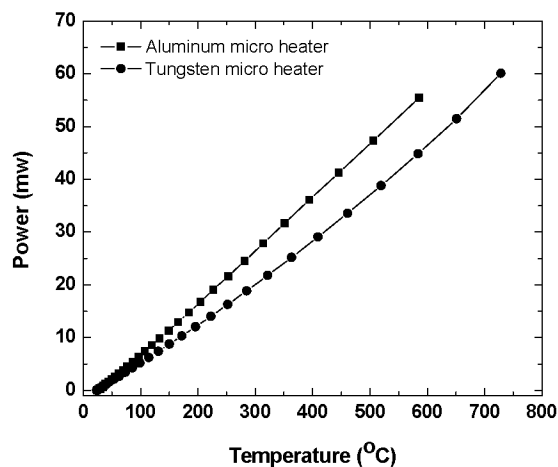


Fig. 3. Power versus temperature plots of aluminum and tungsten micro heaters.

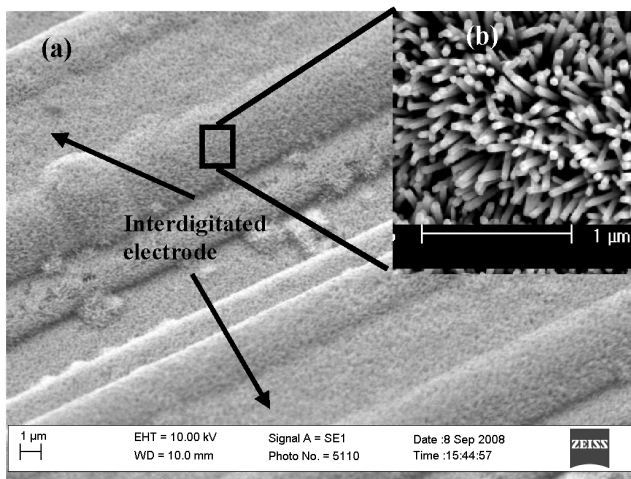


Fig. 4. (a) Top view of the SEM images of the ZnO NWs on interdigitated electrode, (b) zoom in view of NWs.

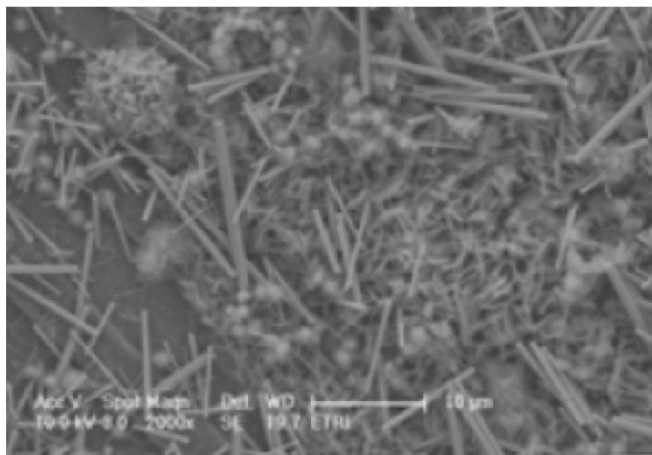


Fig. 5. SEM image of the deposited ZnO nanowires [46]

In the case of CNTs the sensing principles proposed by different groups are somewhat less rigorous and leave room for a more comprehensive understanding. The largest number of reported CNT based gas sensors target NO_2 and NH_3 gases. Several groups have attempted [49-53] to explain the sensing mechanism of Carbon Nanotubes (both SWCNT and MWCNT) when exposed to NO_2 and NH_3 . Some theoreticians have used different tools (e.g. DFT calculation [50], self consistent field electronic structure- calculation [51], self consistent charge density functional based tight binding method [54] etc.) to figure out binding affinities between CNTs and NO_2/NH_3 and hence to devise a favorable mechanism that will be consistent with the experimental results. The popular two mechanisms are (i) physisorption and (ii) chemisorptions. In the case of physisorption physical adsorption (probably due to van der Waal forces) of gases (e.g. NO_2) takes place onto the

sidewalls of CNTs leading to the formation of new states near the CNT Fermi levels that cause the change in resistance of the nanotubes. Whereas, in the second case, adsorbed molecules form bond structures with nanotube defect states and thus change the conductance of the CNTs.

GAS/VAPOUR TEST RESULTS

The response of the sensor is defined in this work as $[(R_b - R_a)/R_a] \times 100\%$ where R_a is the baseline resistance of nanomaterial in presence of humid air/dry nitrogen and R_b is the resistance in presence of target gas or vapour.

The response of the MWCNT-based sensors was investigated for NO_2 gas, which was balanced with dry N_2 carrier gas fixed at 1000 sccm [55]. The sensor was

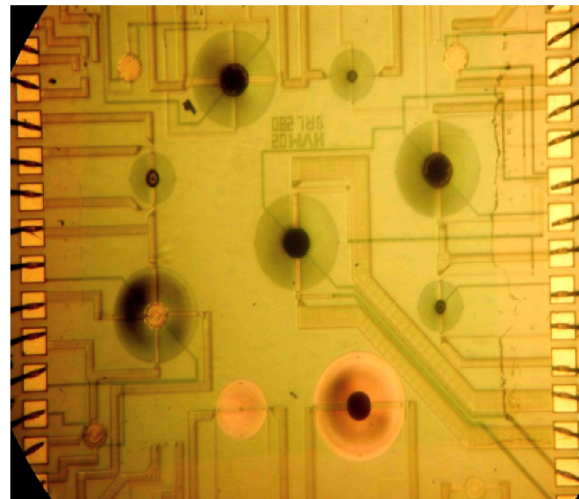


Fig. 6. Optical microscope picture of the locally grown MWCNTs on a fully processed CMOS chip.

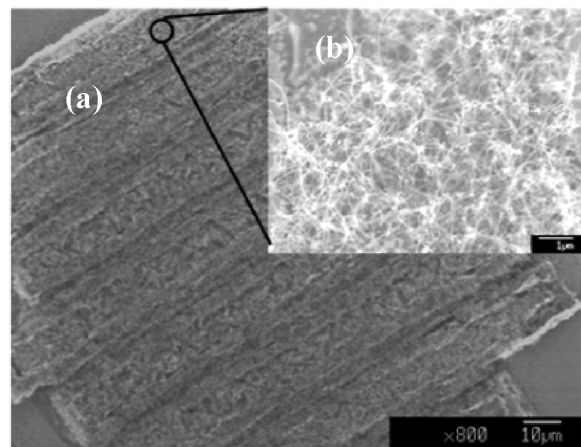


Fig. 7. (a) SEM pictures of the locally grown MWCNTs on interdigitated electrode, (b) zoom-in view of MWCNTs.

found to offer a response of 8 % to 100 ppb (parts per billion) of NO₂ and 20% at 20 ppm (parts per million) at room temperature before falling off at lower concentrations (Fig. 8). Following the removal of NO₂, the embedded micro-heater was used to speed up the recovery time (facilitate NO₂ desorption). 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 quickly the baseline resistance. At higher temperatures the sensitivity is lower but no refreshing is required at an elevated temperature of 270°C for baseline recovery so there is a slight trade off between sensitivity and reversibility. To operate at elevated temperatures and/or refreshing the baseline at high temperatures, the micro-heater (placed underneath the sensing material region) was used for local heating with very low power consumption.

The sensing response of ZnO nanowire sensors were also investigated in the presence of NO₂ using the above mentioned setup [46]. Sensing and refreshing was performed at 18 and 25 mW, respectively. For this, the sensors were heated locally using the integrated tungsten micro-heaters. The measured gas response was shown in Fig. 9. In this case the response was found 40% at 100 ppb of NO₂ and the detection limit can be down to ppb level.

The ZnO NWs response at different ethanol concentrations (175 – 1484 ppm) were also measured, as shown in Fig. 10 [56]. These measurements were

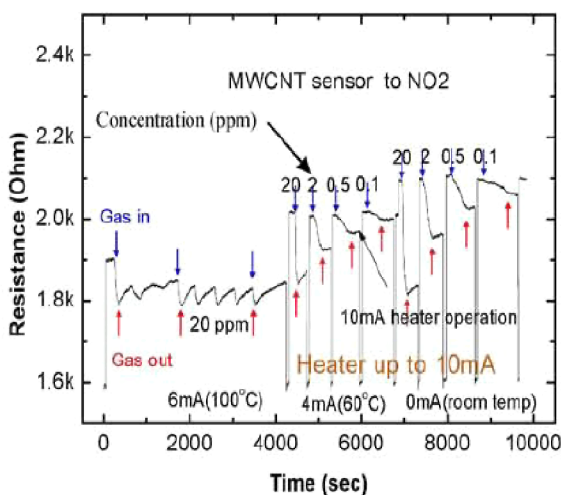


Fig.8. Response of CNTs to 20, 2, 0.5, 0.1 ppm of NO₂. The response time was in the order of minutes, and the of ethanol vapor from the system, recovery of the ZnO NWs was observed to take few tens of minutes before their resistance gets back to the base line value [55].

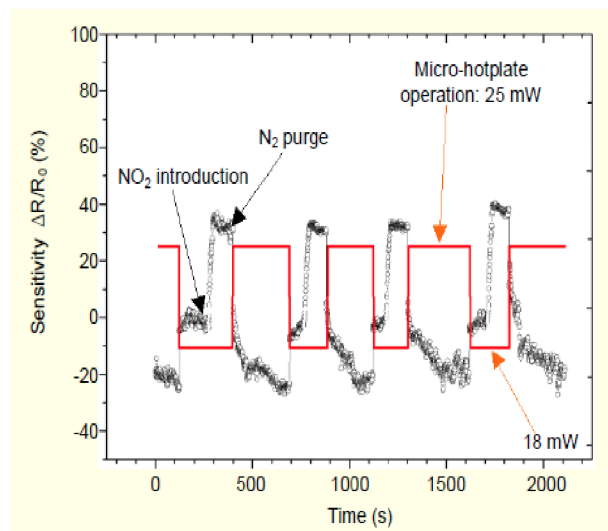


Fig. 9. Response of a ZnO nanowire-based sensor to NO₂ [46].

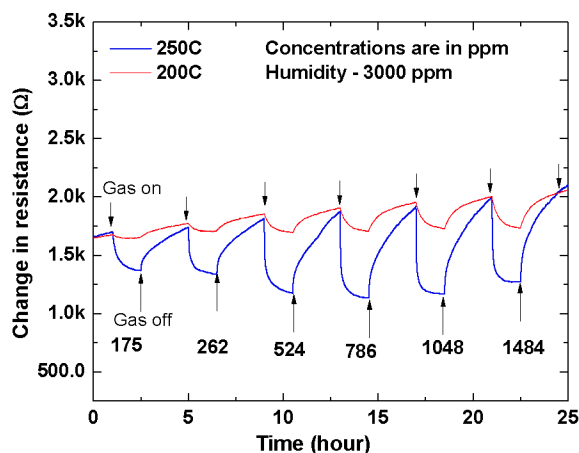


Fig.10. Change in resistance of the fabricated ZnO NWs ethanol gas sensor at different temperatures and different concentrations at a constant humidity of 3000 ppm [56].

carried out at five different concentrations of ethanol vapour in humid air. Humidity was kept constant at 3000 ppm throughout. This measurements were performed at 200 and 250°C (18 and 22 mW) using local micro-heater. We found that the response of NWs to ethanol vapour is significant and takes place within a few minutes.

DISCUSSION AND CONCLUSIONS

In this paper we presented the status of nanomaterials for gas sensing applications. We have paid particularly attention to issues related to growth

compatibility, to CMOS processes and materials. We have given examples of the growth/deposition of ZnO nanowires and CNTs onto CMOS substrates. We covered briefly the gas sensing mechanisms reported in the literature and we have presented the response of ZNO NW and CNTs grown/deposited onto CMOS microhotplates to gases and vapours.

Nanomaterials with higher sensitivities (due to high surface to volume ratio) and higher selectivities (by functionalising or doping) are likely to form a new, future class of microsensors. Such nanomaterials need to be integrated with CMOS to get all the advantages of the conventional ICs (intelligence, cost, high volume, use of low power consumption microhotplates etc). However, the production of such sensors remains very challenging because of the requirements of respective fabrication steps of nanomaterials (which often need harsh environments) and the limitations imposed by the microelectronics technology. While the latter represents a hurdle that can be overcome at present, the former remains an issue to be addressed in the future. Such fabrication steps and recipes should deliver nanomaterials that are highly stable, selective and very importantly, reproducible.

Of the two materials discussed in this paper, ZnO nanowires have the advantage that they can be grown at lower temperatures using the hydrothermal methods. This growth method is more suitable for CMOS substrates compared to the local growth method for CNTs which requires high temperatures above 700°C, or for other metal oxide NWs that typically require high growth temperatures. CNTs, however, can instead be deposited by an inkjet printing or using a spray coating technique.

During operation, CNTs have the advantage of requiring lower operating temperatures, or even room temperature – compared to much higher temperatures required for ZnO NWs. This results in lower power consumption, making the sensors more suitable for portable and wireless applications.

However, these and other materials still need more study. For example, there are very few studies on the effects of dynamic environments with interfering species, long term stability and reproducibility (as already mentioned). Furthermore, most of the R&D works on chemical sensors using nanomaterials report excellent individual gas sensing performance, where the sensor measurements were carried out either in dry air, dry inert gas (e.g. Ar) or even in vacuum. Unfortunately this is far from real sensors' working conditions where humidity, presence of interfering gases, changes in ambient temperature etc. play a crucial role. Hence the effects of these factors also need to be carefully considered when evaluating sensing materials before these are deployed in real world applications.

The future of nanomaterial based sensor technology with CMOS integration looks promising, and we see continuous progress in this field. There are however numerous challenges that need to be overcome before such sensors can make it in the market.

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