A new approach to gas sensing with nanotechnology

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Nanosized gas sensor elements are potentially faster, require lower power, come with a lower limit of detection, operate at lower temperatures, obviate the need for expensive catalysts, are more heat shock resistant and might even come at a lower cost than their macro-counterparts. In the last two decades, there have been important developments in two key areas that might make this promise a reality. First is the development of a variety of very good performing nanostructured metal oxide semiconductors (MOSs), the most commonly used materials for gas sensing; and second are advances in very low power loss miniaturized heater elements. Advanced nano- or micro-nanogas sensors have attracted much attention owing to a variety of possible applications. In this article, we first discuss the mechanism underlying MOS-based gas sensor devices, then we describe the advances that have been made towards MOS nanostructured materials and the progress towards low-power nano- and microheaters. Finally, we attempt to design an ideal nanogas sensor by combining the best nanomaterial strategy with the best heater implementation. In this regard, we end with a discussion of a suspended carbon nanowire-based gas sensor design and the advantages it might offer compared with other more conventional gas sensor devices.

Keywords: gas sensor; carbon nanowire; biosensor; nanowire sensor; chemical vapour deposition

1. Introduction

Over the past five decades, there has been an increasing demand for inexpensive, accurate, portable and reliable gas sensors that can discriminate between very low concentrations of analytes. Typically, gases of interest include CO, NO, NO2, NH4, SO2, CO2, CH4 and other hydrocarbons. These gases can be harmful to human health if present beyond a certain concentration. Historically, gas sensors were first primarily used in coal mines where accurate monitoring of hazardous gases has to be carried out continually. Soon gas sensors were also beginning to

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Gas sensors appear in the chemical industry, in environmental pollution monitoring units and in the human health sector. Some other important applications of gas sensors include the analysis of organic vapours, such as toluene, methanol and benzene, for laboratory and industrial safety [1] and, breath analysis for traffic safety [2] and disease diagnosis [3]. An electronic nose, based on arrays of gas sensors [4] for testing the smell of food, perfumes and artificial fragrances etc., is one of the more recent embodiments of gas sensing that has received much attention owing to its enhanced analytical power.

The performance of a gas sensor is foremost measured by its lower limit of detection (LOD) and by its selectivity. The gas sensor with the lowest LOD is the one that affords the detection of the lowest level of an analyte and a highly selective gas sensor enables the detection of very minute amounts of the desired gas in a mixture of several other gases. Low power consumption, fast response and recovery time, stability (low drift rate) and sensitivity, i.e. the slope of the sensor output versus the analyte concentration, are other important sensor performance characteristics.

Gas sensors can be classified based on the detection mechanisms involved and the type of materials used in their manufacture. They may be based on a wide variety of detection mechanisms, such as changes in optical absorption or fluorescence [5] modulation of the field in field-effect transistors [4], changes in surface acoustic wave propagation [6], electrochemical phenomena (e.g. voltage changes in potentiometry [7,8] or current change in amperometry [9]) and, resistance changes in metal oxide semiconductors (MOSs) [10]. In terms of gas sensor materials, metal wires and films were employed as sensing elements in some of the very first gas sensors, but polycrystalline MOSs dominate gas sensor construction today. Metal catalysts such as Pt and Pd are often mixed with these semiconductor materials to catalyse gas sensing through the spillover effect that is explained later in this article.

The measuring principle of the gas sensors we focus on in this contribution is that of electrical conductivity changes of heated MOS layers as a function of the composition of gases present in the atmosphere surrounding the sensing element. The MOS gas-sensing materials are typically n-type semiconductors that under normal atmospheric conditions and typical working temperatures of 300–600°C develop an electron-depleted surface layer. This electron depletion layer is caused by atmospheric oxygen that at high temperature adsorbs on the surface and ‘steals’ electrons from the MOS film surface to form reactive O$_{2}^-$ or O$^-$ species. The presence of gases in the surrounding atmosphere that react with the reactive oxygen species at the MOS surface modulates the depletion layer thickness, and this leads to measurable changes in the resistance of the material. Reducing gases like CO and H$_2$ react with the highly sensitive MOS surface and remove some of the chemisorbed oxygen while injecting electrons back into the MOS, which causes a reduction in the thickness of the depletion layer. Oxidizing gases such as NO$_2$, on the other hand, ‘steal’ even more electrons from the solid, thereby increasing the thickness of the depletion region [11]. Any such microscopic changes in the depletion layer thickness affect the overall resistance of the MOS material, which is measured using simple and inexpensive electrical circuitry.

To achieve selectivity in these types of gas sensors, the required operating temperature is usually between 300°C and 600°C; at these temperatures, chemisorption becomes more important than physisorption and chemisorption
is by far the more selective process. In the gas sensor community, we instinctively know that fact: physisorbed water converts almost every material operating at low temperature into a humidity sensor [12]. Therefore, the sensing unit must feature a heating element that provides the desired temperature for adsorption and desorption of oxygen gas and for reaction of the analyte gases with those reactive adsorbed oxygen species. The reactions at the heated MOS surface change the concentration of electrons in the MOS film depletion layer, and this in turn changes the conductance of these devices as a function of gas concentration. These gas-induced resistance changes are influenced by many material-related factors such as the type of semiconductor oxide material, oxide film thickness, grain size, porosity, material sintering temperature and time, catalyst type and catalyst particle distribution.

In an optimized gas sensor design, the power consumption should be as low as possible and the heat losses owing to convection, conduction or radiation by the heater should thus be minimized. To minimize the power consumption, one needs to reduce the mass of both the heater and the sensor element and optimize the design for uniformity of heating. Both the heater and the sensor material are obviously strongly influenced by miniaturization. With the advancement of micro- and nanofabrication techniques, sensors evolved from small catalytic bead platinum wire detectors and Taguchi gas sensors to micro- and nano- solid-state gas-sensing devices.

In this contribution, we first discuss the effect of downscaling on sensing materials and on heater elements and then suggest possible ways to integrate optimized nanomaterials and nanoheater elements. The latter will be illustrated with an example of a suspended carbon nanowire (CNW)-based gas sensor design conceived in our laboratory. We believe that this newly conceived sensor will become the basis for many types of new gas sensors for biological and biomedical applications.

2. Sensing materials: effect of grain size and film thickness

The most traditionally used materials for solid-state gas sensors are thick films of polycrystalline compressed or sintered MOS powders. In the case of compressed powders, the grain-boundary resistance dominates the response of the sensor device since the resistance at these intergranular contacts is much larger than the resistance across a single grain. Compressed powders are not very stable as the intergranular contact is pressure sensitive. In sintered powders, some of these grain boundaries disappear and form more stable neck-like structures as the grains sinter together. These necks often constitute the most sensitive sites of sensing materials as all the electrons from these narrow necks are potentially tied up with the adsorbed oxygen, giving rise to very sensitive completely electron-depleted highly resistive regions.

In figure 1, we illustrate the energy band model for an MOS compressed powder. A few grains are shown where chemisorbed oxygen has captured electrons from the material forming a depletion layer (also known as the space charge layer or the Debye layer). At the intergranular contact, two space charge layers back-to-back form a formidable barrier for electrons to cross, and this gives rise to the higher resistance values at those contact points. The thickness of the depletion
layer or the Debye layer ($L$) is relatively small compared with the grain diameter ($D$) in most traditionally polycrystalline materials. A typical value for $L$ is 100 nm for MOS films [12]. Grain-boundary-controlled gas sensing, most important for relatively large-particle MOS sensors, has been extensively reviewed by Barsan and Weimar [13,14]. In this contribution, we use these early sensing models to gain an understanding about what to expect when particle size decreases to the nanometre range.

When an MOS gas sensor is exposed to reducing gases, such as $\text{H}_2$, $\text{CO}$ and $\text{CH}_4$, at a sufficiently high temperature, the chemisorbed oxygen reacts with the reducing gases, lowering the steady-state surface coverage of the oxygen while injecting electrons into the MOS crystallites and thus lowering the height of the potential barriers at the intergranular contacts ($qV_s$ in figure 1). The important reactions involved in this type of gas sensor may thus be summarized as follows.

Oxygen reactions

$$\text{MO} + \text{O} + e^- \rightarrow \text{MO} - \text{O}^- \quad \text{(between 150°C and 300°C)} \tag{R 1}$$

$$\text{MO} + 2\text{O} + e^- \rightarrow \text{MO} - \text{O}_2^- \quad \text{(between 30°C and 150°C).}$$

As a result, electrons are extracted and resistance goes up.
Reducing gas reactions

Reducing gas molecules (R) react with the chemisorbed oxygen at the grain boundaries and/or necks,

\[ \text{R} + \text{MO} - \text{O}^- \rightarrow \text{MO} + \text{RO} + \text{e}^- . \]  \hspace{1cm} (R 2)

As a result, electrons are injected and resistance goes down.

Also, oxidizing gases can be detected. The oxidizing reactions may be summarized as

\[ \text{MO} - \text{O}^- + \text{O} + \text{e}^- \rightarrow \text{MO} - \text{O}_2^- . \]  \hspace{1cm} (R 3)

As a result, electrons are extracted and resistance goes up even further. Therefore, by measuring the change in the conductivity of the semiconductor oxide films, one can detect reducing and oxidizing gases in the atmosphere.

The above analysis of the MOS sensing mechanism, for the sake of clarity and brevity, is somewhat simplified. Indeed, not only a change in the number of free electrons (and thus boundary layer thickness modulation) but also changes in electron mobility may modulate the sensing response, as investigated by Ogawa et al. [15] and recently reviewed by Tricoli et al. [16]. Furthermore, there is still an ongoing debate in the MOS gas sensor community about the possibility of another sensing mechanism altogether. Gurlo & Riedel [17] point out that, although it has been sought for a long time, there is not yet any convincing spectroscopic evidence for oxygen ‘ionosorption’ as shown in figure 1. In their alternative model, there is no oxygen ionosorption on the MOS surface and the model focuses instead on oxygen vacancies at the surface, which are considered to be ‘the determining factor in the chemiresistive behavior’ [18]. SnO₂, the model gas-sensing material, is oxygen deficient and therefore acts as an n-type semiconductor, with oxygen vacancies that act as electron donors. Alternate reduction and reoxidation of the surface by gaseous oxygen control the surface conductivity and therefore the overall sensing behaviour in this model.

Catalysts such as Pt enhance gas-sensing reactions of MOS via the spillover effect. Spillover refers to the process in which the catalyst dissociates a gas molecule and then the atoms ‘spill over’ onto the surface of the MOS. At the right temperature, a gas reactant first adsorbs onto the surface of the catalyst particles and then migrates to the oxide surface to react there with reactive surface oxygen species. For this process to be possible, the spilled-over species must be able to migrate to the interparticle contact (grain boundary or neck). As a consequence, for a catalyst to be effective, there must be a very good dispersion of the catalyst particles so that they are available near all contacts. Only then can the catalysts affect the interparticle contact resistance that controls the gas sensor sensitivity. Importantly, in the case of nanoparticles, there are several reports which indicate that the need for metal catalysts is somewhat alleviated [19,20].

Porosity, grain size and film thickness all play an important role in the LOD and sensitivity of MOS gas sensors. Lee et al. [21] carried out a comparative study of thick- and thin-film SnO₂ gas sensors in order to understand the differences in gas-sensing characteristics as a function of the microstructure of the gas-sensing materials. Thin films, in their investigation, were deposited using metal organic chemical vapour deposition (CVD), which yielded a dense compact microstructure (figure 2). Thick porous films were derived from metal organic decomposition. These thick films were made up of a network of loosely connected...
crystallites that also featured several cracks (approx. 1 μm wide, [21]) as well as small pore channels at the crystallite surfaces that all help in the penetration of gas molecules throughout the material and thereby enhance the sensitivity (figure 2). Lee et al. confirmed a much improved gas sensitivity in the case of porous thick-film microstructures compared with compact thin layers of SnO₂. In a porous MOS film, grain boundaries are present in all directions and more surface area is available for reactions (R 1)–(R 3) to take place. In a compact film, on the other hand, only a limited exposed surface area is affected by the presence of analyte gases. Therefore, porous films are superior for gas-sensing purposes. In figure 2, we illustrate the surfaces that are likely to participate in the resistance change of these two types of MOS gas-sensitive material configurations.

Since the sensitivity of the high-surface-area porous gas sensors resides in the high resistivity grain-boundary contact points, one wants to make the number of these contact points as high as possible. So a thicker porous film is better. One also wants to make these contact points as stable as possible. A powder that is not sintered is pressure sensitive and quite unstable. In order to improve this, the MOS powders are sintered, giving rise to the formation of necks between the grains in the powder. The sensitivity of the film depends very much on the extent of the sintering of the material. One should not sinter so much that the film becomes one compact layer, reducing the porosity and thus the sensitivity of the sensor dramatically. In most sintered MOS films, both necks and grain contacts are present. Neck–grain models with different degrees of neck formation have been investigated by several research groups.

Xu et al. [22] proposed a model with a chain of crystallites connected mostly by necks and sometimes by grain-boundary contacts. These authors assumed neck size \( X \) 0.8 times the crystallite size \( D \) and suggested that, when \( D \) is larger than \( 2L \), grain-boundary contacts display higher resistance and govern the electric gas sensitivity of the chain (grain-boundary control). As \( D \) becomes smaller and comparable to \( 2L \), necks become most resistant and therefore they start controlling the gas sensitivity (neck control). Finally, when \( D \) is smaller than \( 2L \), the resistance of grains dominates the whole resistance of the chain and the gas sensitivity in this case is controlled by grains themselves (grain control) and yields
Figure 3. Schematic models for grain-size effects (adapted from [23]).

the largest gas sensor response. Figure 3 demonstrates the three situations. Along the same line, Rothschild and Komem [19] showed that the gas-induced variations in the trapped charge density in the MOS are proportional to $1/D$, where $D$ is the average grain size. At the nanoscale, the grain size can be decreased to match the Debye layer ($L$) thickness (typical value is 100 nm—see above), or can even be made smaller, which leads to the extraction of all electrons by the chemisorbed oxygen present. Such nanostructures can thus be treated as gas sensor materials with uniformly changing resistance upon exposure to gases (see grain control in figure 3).

Ma et al. [24] carried out a theoretical study to better understand the dependence of the grain-boundary potential barrier as a function of the density of electrons trapped at the surface ($n_t$) and electron density in the bulk of the material ($n_b$). These authors suggest a model for neck–grain boundary control in order to investigate the combined effect of neck and grain boundaries in a sintered powder. For a constant distribution of such donors, the height of the grain-boundary potential barrier ($eV_s$, see figure 1) is

$$eV_s = \frac{e^2 n_t^2}{2 \sum_0 \sum_r n_b}, \quad (2.1)$$

where $e$ is the electron charge, $n_t$ is the surface electron density, $\sum_0 \sum_r$ is the permittivity and $n_b$ denotes the free electron density in the grain body.

Assuming that the necks in a sintered ZnO powder are cylindrical, resistance values were calculated for both neck and grain boundaries employing equation (2.1). Like Xu et al. [22], these authors concluded that gas sensitivity increases with decreasing grain size, which results from increased neck control. From this discussion, we can also appreciate that, in the case of a thin compact film, one likes the thickness to be small, perhaps in the range of $L$ or less, so as to have a completely electron-depleted thin film.

We can conclude from the discussions so far on grain size, porosity and thickness that, for the best gas sensor performance, we need a thick film of lightly sintered nanocrystalline, porous material. Nanocrystalline metal oxides offer other
advantages as well; they can operate at lower temperatures and might obviate the need for expensive catalysts [25]. Some words of caution are in order here with respect to the ultimate MOS grain size and the optimal film thickness.

Nanomaterials do indeed not come without disadvantages. Especially, thermal instabilities are worrisome since smaller MOS grains tend to agglomerate at lower temperatures, and this leads to changing sensor characteristics over time. Thermal degradation is responsible for temporal instabilities in device parameters and higher drift rates. According to Korotcenkov & Cho [26], the larger the grain size, the wider the temperature range in which crystallites retain their size and shape without changes. Conversely, the smaller the grain size, the lower the temperature at which structural changes start taking effect; for example, films with a grain size of 2–3 nm start transforming at temperatures of approximately 200 °C. The same authors concluded that very small (approx. 20 nm) particles of SnO2 and In2O3 MOS materials are not quite suitable for gas sensing above 500 °C, as the particles melt and agglomerate at much lower temperatures than their respective bulk melting points. An optimum approach that balances a high sensitivity by decreasing the particle size with good stability, calibration frequency and lifetime requirements of a commercial gas sensor is therefore recommended. A few words with respect to optimum film thickness. Above, we advocated making porous, lightly sintered nanoparticles into a thick film for the ideal gas sensor characteristics. On the other hand, some reports have shown that reducing the film thickness does increase the sensor’s response considerably [27]. This is in agreement with models of MOS sensor response to several analytes [28] and has been discussed in detail recently by Tricoli et al. [16]. Without more detailed studies, this is a hard argument to settle; indeed particle size, degree of sintering and thus porosity are all intertwined. Depending on the porosity and particle size, either a thinner or a thicker film might be required.

MOS nanocatalysis can be considered as a bridge between homogeneous and heterogeneous catalysis. Because of their nanosize, i.e. high surface area, the contact between reactants, gas sensors and nanoparticles is huge. Pinna et al. [29], for example, demonstrated that gas sensors based on tin and indium oxide nanopowders exhibited high sensitivity and good recovery time at low temperature. Especially, indium oxide nanoparticles were highly sensitive towards NO2 with a detection limit of 1 ppb at low temperatures.

Nanobelts (nanowire-like structures but with flat cross sections) [30], nanorods [31] and nanowires [32] have all been successfully implemented as gas sensor materials and continue to be investigated for their potential advantages over traditional materials. These nanomaterial-based gas sensor devices are based either on mass assemblies of nanoparticles (e.g. porous mats) or on one or a set of individual nanoparticles (e.g. a small number of nanowires).

Sadek et al. [30], for example, developed a conductometric H2, NO2 and hydrocarbon gas sensor using a ZnO nanobelt film as the sensitive layer. In Sadek et al.’s experiments, ZnO nanobelts display a structural morphology (wurtzite family) characterized by a rectangular cross section and a uniform long structure along their length. A mat of these nanobelts was deposited by radio frequency (RF) sputtering on a heater element.

The sensing elements in sensors fabricated by Lee et al. [31] are thin films consisting of SnO2 nanorods. The nanorod films also were equipped with well-dispersed Pd catalyst nanoparticles with an average diameter of 3 nm. These
thin-film nanorods were deposited using plasma-enhanced CVD (PECVD) with post-plasma treatment. The surface of these nanorod thin films was modified with Pd nanoparticles, and the sensing properties of the thus fabricated films were tested with H₂ and ethanol vapours. Yeom et al. [33] employed nanomembranes for pre-concentration of gases that were detected using a microfluidic sensor that resulted in much enhanced sensitivity.

In another study by Liu et al. [34], vanadium oxide nanobelts coated with MOS nanoparticles such as Fe₂O₃, TiO₂ and SnO₂ were employed as hybrid sensor nanostructures for sensing ethanol vapours. These vanadium pentoxide (V₂O₅) nanobelts coated with MOS nanoparticles showed a much improved sensitivity compared with the nanobelts alone. The authors suggest that the coated V₂O₅ nanobelts exhibit enhanced sensitivity owing to the synergy between electrical transport through the largely depleted nanobelts and the effective gas sensing on the high surface area MOS nanoparticles that inject electrons into the nanobelts. The V₂O₅ nanobelts were synthesized using a chemical process based on a mild hydrothermal reaction of 0.1M ammonium metavanadate solution in dilute nitric acid, and the MOS nanoparticle coatings were fabricated from ferric nitrate, tetrabutyl titanate and tin tetrachloride in ethanol, for depositing Fe₂O₃, TiO₂ and SnO₂, respectively. The sensing mechanism is clarified in figure 4 with a schematic drawing of a longitudinal cross section of nanobelts coated with MOS nanoparticles.

Upon exposure to ethanol, the electron-depleted surface layers in both the nanobelts and the nanoparticles are reduced because of the electron injection that accompanies the reaction of ethanol with the reactive adsorbed oxygen species. The authors believe that the boundaries between metal oxide grains on the V₂O₅ nanobelts dominate the sensor resistance.

As micromachined heater elements tend to be mechanically less sturdy than the ceramic substrate-based heaters in traditional gas sensors (§3), we also need to pay close attention to how the MOS nanoparticles are deposited. Techniques that do not exert mechanical pressure on the brittle micromachined heater substrates and result in porous nanoparticle films constitute the more attractive technologies. RF sputtering, for example, as used by Sadek et al. [30] (see above), is a possible approach but the process needs to be modified so as to generate more porous films.

As another example, Cukrov et al. [20] synthesized tin oxide nanoparticles (average diameter 24 nm) and tested the O₂ sensing properties of porous thin films prepared by mechanochemical processing and spin coating. The mechanochemical process uses a conventional ball mill in which the mechanical energy activates the necessary chemical reactions and induces structural changes. Figure 5 shows a transmission electron micrograph of tin oxide nanoparticles fabricated by this mechanochemical method. These particles were subsequently spin coated in a thin film on alumina substrates with interdigitated electrodes (measuring electrodes on the front side and the heater on the back side). These films were tested for their oxygen-sensing potential and were found to be extremely stable and repeatable. Although the nanomaterial is very interesting because it does not require any metal catalyst and because of its demonstrated stability, spin coating is not a method of choice to coat the MOS on fragile microelectromechanical system (MEMS) or nanoelectromechanical system (NEMS) structures. Screen printing of electrodes and sensing materials, as often employed in the construction of...
Figure 4. Schematic of the ethanol-sensing mechanism of vanadium oxide sensors coated with SnO₂, TiO₂ and Fe₂O₃ [34].

traditional gas sensors, is an even less attractive candidate as significant pressure is exerted on the substrate in the silk screen printing [35]. During screen printing, pressure is exerted on the structures [36] and therefore it may not be a very useful technique for fabricating fragile nanogas sensors.

Another nanopowder gas sensor, based on the synthesis of Al-doped TiO₂ nanoparticles (average diameter 100 nm), was reported by Choi et al. [37]. The nanopowder in this study was used to make thick-film gas sensors to measure CO selectively and sensitively in an O₂ environment. A thick film of this material was prepared on an alumina substrate with interdigitated Pt-measuring electrodes. To integrate the material with the measuring electrodes, the nanopowder was mixed in an appropriate solvent (alpha terpineol) and, drop by drop, was deposited on the electrodes followed by drying and densifying, at 100°C and 800°C, respectively, on the thus deposited films. This chemical method as well as sol–gel techniques and physical vapour deposition [35] (see RF sputtering used by Sadek et al. [30]) are all feasible approaches to integrate sensing materials on brittle MEMS and NEMS structures. An especially attractive approach to deposit MOS locally on a brittle heater structure is to use the heat of the heater element itself to initiate the CVD from a metallo-organic precursor. Such an approach was pioneered by Cavicchi et al. [38], who deposited films on the prefabricated gas heater structures employing thermally activated CVD.
Figure 5. Transmission electron micrograph of tin oxide nanopowder [20].

Figure 6. Basic outline of the CVD technique [35].

In CVD, a controlled mixture of precursors is brought in contact with a heated substrate, which causes a chemical reaction between the vapour and the substrate and leads to the deposition of a layer of the desired compound on the substrate. A basic outline of the CVD method is illustrated in figure 6.

Commonly employed CVD techniques include atmospheric pressure CVD (APCVD), aerosol-assisted CVD (AACVD), PECVD and rapid thermal CVD. An advantage of using CVD for gas sensor purposes is that the thickness
and density of the film can be optimized by controlling the concentration of the reagents in the vapour and the time of deposition. A concentrated vapour precursor yields a compact film that may grow at a rate of up to $1 \mu m \text{min}^{-1}$; a rarified mixture of reagents on the other hand deposits a more porous film at a considerably lower growth rate [35].

Two relevant CVD applications are by Shaw et al. [39] and Ashraf et al. [40]. Shaw et al. [39] employed AACVD for the deposition of tungsten oxide from $\text{W(OPh)}_6$ (the precursor) in toluene at $600^\circ\text{C}$. After a deposition time of 90 min, a 50–75 nm thick fibrous film was obtained. The thus fabricated films can be made thicker by using an electrical field in the CVD process. The authors investigated the porosity of the tungsten oxide films, a feature, as we know, of key importance for the utility of these films in gas sensing, at different applied voltages.

Ashraf et al. [40] demonstrated that APCVD is an effective technique for depositing tungsten films as thick as 3.6–6.7 $\mu m$. They used $\text{WCl}_6$ as the precursor vapour and operated the reactor at $625^\circ\text{C}$ in $\text{N}_2$. The particles in these up to 6.7 $\mu m$ thick tungsten oxide films were thin needle-like crystals with a high surface area and high porosity. Significantly, Ashraf et al. found that the MOS films deposited this way are more sensitive than those fabricated by screen printing.

One of our preferred nanogas sensor designs described in §5 is inspired by the gas sensor configuration shown in figure 4. In our design, we deposit an MOS on a suspended CNW that we use as both a heater and a sensing electrode. The CVD deposition is initiated by ohmic heating of the CNWs (as in the case of the microhotplates shown in figure 8).

Carbon nanotube (CNT)-based miniaturized gas sensors constitute yet another innovation in nanogas sensing. A single-walled CNT is a one-molecule-thick layer of graphite rolled into a cylinder with a diameter of a few nanometres. Multi-walled CNTs are composed of several such graphite cylinders rolled up into one. The distribution of electrons on their outer surface only makes CNTs extremely sensitive to charge transfer and chemical doping effects by surrounding molecules [41,42]. When electron-withdrawing or electron-donating gas molecules come in contact with CNTs, it very dramatically changes the surface electron concentration. CNT-based gas sensors show faster response, higher sensitivity and lower operating temperatures and detection ability for a wider variety of gases than any other gas-sensitive material [43]. Because of these extensively perceived advantages, the use of CNTs, both pristine and functionalized, continues to be studied extensively. Unfortunately, the difficulty in making electrical contact to CNTs and the tremendous variety of lengths, thicknesses and conductivities they come in have hampered progress. Our approach to nanogas sensing with suspended CNWs (§5) constitutes a viable alternative to CNT-based gas sensing as we can control contact resistance, thickness and resistivity of the nanowires very well.

3. Miniaturization of heater elements in gas sensors

As we discussed above, most MOS gas sensors operate at temperatures above $300^\circ\text{C}$ and, even though nanopowders enable lower operating temperatures, a heater remains mandatory. Operating at higher temperatures improves selectivity and reduces the effect of humidity, or stated more generally: chemisorption prevails over physisorption at higher temperatures. For this purpose, an MOS film
is typically heated using an integrated heating element that facilitates the desired exchange of electrons between chemisorbed oxygen and the MOS, and between the analyte gas and the active oxygen species on the MOS surface (see reactions R1 and R3). To design a good heater element, one wants to minimize power consumption, make the heater rugged enough so that a gas-sensitive material can be readily applied to its surface and avoid temperature gradients that may lead to thermal cracking of the sensor and—in case one relies on a modulated temperature profile for gas sensing—one also wants the sensor response time to be fast.

Two important dimensionless numbers provide zeroth-order guidance for designing heaters that meet the above thermal requirements. First is the dimensionless \textit{Biot number}, defined as the ratio of the surface heat-transfer coefficient over the bulk heat conductivity (equation (3.1)). The larger the Biot number, the higher the accumulated heating stress in the heater element and thus the more real the danger of the heater element cracking,

\[ Bi = \text{Biot number} = \frac{\lambda L}{\kappa}, \quad (3.1) \]

where \( L \) is the characteristic length, \( \lambda \) is the heat-transfer coefficient at the surface and \( \kappa \) is the bulk heat conductivity.

From equation (3.1), we understand that the Biot number is directly proportional to the characteristic length \( L \) (or also to the volume to surface area \((V/A = L)\)) of the heater. Values of the Biot number smaller than 0.1 imply that the heat conduction inside the body is much faster than the heat convection away from its surface, and temperature gradients are negligible inside of it; in other words, thermal stresses do not accumulate easily in large surface area to volume structures (such as small heaters). This constitutes a tremendous advantage for micromachined heating elements; with a very low Biot number, these devices can be heated and cooled faster than large heater elements without any risk of thermal-stress-induced cracking.

A second dimensionless number that correlates heat transfer in a body with its size is the \textit{Fourier number} (equation (3.2)). This is the ratio of the heat conduction rate to the rate of thermal energy storage. It is used in the description and prediction of the temperature response of materials undergoing transient conductive heating or cooling,

\[
F_o = \frac{\kappa t}{\rho C_p L^2} = \frac{\alpha t}{L^2} = \frac{\kappa}{\rho C_p L^2}, \quad (3.2)
\]

where \( \alpha \) is thermal diffusivity, i.e. the bulk heat conductivity divided by the volumetric heat capacity \( C_p \), and the material density \( \rho \); \( t \) is the characteristic time and \( L \) is the characteristic length through which conduction occurs. Calculations based on the Fourier number suggest that a 10 times reduction in size leads to \( 10^2 = 100 \) times reduction in time to heat or cool the solid. In other words, downscaling leads to faster heating or cooling.

The Fourier and Biot numbers can be used in transient conduction problems in a lumped parameter solution which show that the difference between the
temperature of the system and its surroundings \((= \Delta T)\) as a function of time \(t\) is given by

\[
\Delta T(t) = \Delta T_0 e^{-\frac{B t}{t}} = \Delta T_0 e^{t/\tau},
\]

where

\[
\tau = \frac{C_p V}{h A} = \frac{C_p L}{h},
\]

(3.3)

where \(h\) is again the surface heat-transfer coefficient, and \(L\) is the characteristic length \((V/A)\), \(T(t)\) is the body temperature at time \(t\) and \(\Delta T_0\) is the initial temperature difference at time \(t = 0\). It is observed that a larger thermal time constant \(\tau\), caused by larger masses \(\rho V\) and larger heat capacities \(C_p\), leads to slower changes in temperature, while, with larger surface areas \(A\) and with better heat-transfer coefficients \((h)\), a shorter thermal time constant results in faster temperature changes. The thermal behaviour of a heater can also be expressed as a function of just one lumped thermal resistance \(R_T\) and one lumped capacity \(C\). This way, we can rewrite the thermal time constant as

\[
\tau = R_T C.
\]

(3.4)

From equation (3.4), the thermal time constant depends linearly on the thermal resistance and capacity, so that a sensor with a low thermal mass and a small thermal resistance will exhibit the fastest response. A small thermal mass unfortunately also increases the power consumption so a trade-off needs to be made between power consumption and speed of response [11].

From equations (3.1)–(3.4), we understand that smaller heaters accumulate lower thermal stresses and therefore are less prone to cracking, and we also appreciate now that they heat and cool faster. Micromachined gas sensors have to be optimized with respect to the overall power budget as well: especially if one wants to run the gas sensor on batteries, the power requirements should be kept as low as possible. Finally, a uniform distribution of heat within the sensing layer is important for reproducible and long-lasting gas sensors [44].

In a traditional ‘macro’-Taguchi gas sensor, a coiled metal wire is mounted inside a small ceramic tube (9.5 mm long and 3 mm in diameter) and is employed for heating the MOS material that is coated over the electrodes on the ceramic tube surface. Figure 7a is a representative design of these types of ‘macro’-gas sensors. The cylindrical geometry of the sensor shown ensures an even radial heating throughout the gas-sensing material.

A ceramic-based cylindrical gas sensor as shown in figure 7a is quite power hungry (about 800 mW!) and is somewhat cumbersome to mass manufacture. In a typical ceramic planar gas sensor, a metal oxide gas-sensitive layer is screen printed on a flat alumina substrate (e.g. 250 µm thick). On the bottom side of the substrate, a platinum heater, which might be used simultaneously as a temperature sensor, is fabricated. On the top side of the ceramic, an interdigitated sensing electrode pair is screen printed. Then the gas-sensitive layer is screen printed over these sensing electrodes and fired at a temperature of say 850°C. A picture of this type of sensor is shown in figure 7b. This device structure is more amenable to mass manufacturing than the tubular sensor but is still high in power consumption and has the additional disadvantage that the heating profile is less symmetric.
Since heat consumption is proportional to the size of the sensor, miniaturization plays a very significant role in reducing the power requirement of gas sensors. In the past two decades, several efforts have been made to microfabricate small gas sensors with very small heater elements. Semancik & Cavicchi [47], for example, investigated microhotplate arrays. In this case, the micromachined heater is mounted in a thin suspended low thermal mass membrane as illustrated in figure 8. Owing to the small thermal mass of these microhotplates, one can achieve very rapid heating and cooling with very low power consumption; with some hotplate designs, power budgets of 15 mW have been achieved [48,49]. Microhotplates are manufactured using mass production integrated circuit techniques, so it is easier to make them into arrays for electronic noses [4], and their fast heating/cooling behaviour allows for their usage in a temperature scanning mode [50]. Elmi et al. [51] recently demonstrated an ultra-low-power microhotplate that ran at a very low power value of 8.9 mW at 400°C; their device also features an innovative self-insulated layout between the heater and the sensing layer. The CNW-based heaters that we discuss in §5 are expected to have a much lower power budget owing to the extremely small mass of these wires.

To project how nanotechnology could potentially benefit the gas sensor field, we now review the heat loss mechanisms at work in a microhotplate-based gas sensor of the type shown in figure 8 and we analyse what these losses mean for our own proposed suspended nanowire gas sensor structure (§5). In a high-temperature suspended heater-based gas sensor, heat is transferred
along the membrane via heat conduction; above and below the heater membrane it is transferred through heat conduction and convection through the surrounding atmosphere. Finally, we also need to take into account the heat leakage via radiation. The different heat-transfer mechanisms are illustrated in figure 9a.

(a) Conduction, radiation and convection in the air gap of the gas sensor

(i) Conduction

The air gap between the heater and the substrate shown in figure 8 provides for significant thermal insulation and helps minimize the required heating power. The heat transport in this gap can be classified into four categories according to the magnitude of the Knudsen number ($Kn$, the ratio of the mean free path, $\lambda$, of gas molecules to the characteristic length, $L$, i.e. the thickness of the air gap). These four different heat-transfer regimes are the continuum regime ($Kn < 0.001$), the temperature jump regime ($0.001 < Kn < 0.1$), the intermediate or transition regime ($0.1 < Kn < 10$) and the free molecule regime ($Kn > 10$). As the gas pressure $p$ or the characteristic length $L$ is changed, all four of these regimes may be encountered for a given system. In the free molecular regime, the Knudsen number is near to or greater than 1, i.e. the mean free path of a molecule is comparable to the length scale $L$ of the air gap and the continuum assumption of fluid mechanics is no longer a good approximation. In this case, statistical methods must be used. Han et al. [52] computed the heat transfer through this thin air gap in the four different regimes. Curve 1 in figure 9b shows the variation of the conductive heat flux with gap distance as they calculated it. In the temperature jump regime ($0.001 < Kn < 0.1$), $q$ depends on the gap distance $d$ as

$$q = \frac{K(T_1 - T_2)/d}{1 + 4\gamma Kn(2 - 1)/a(1 + \lambda)Pr},$$

where $q$ is the density of the conductive heat flux, $d$ is the air gap width, $Pr$ is the Prandtl number, $Kn$ is the Knudsen number, $\gamma$ is the adiabatic exponential and...
Figure 9. (a) Heat fluxes of a micromachined gas sensor [11]. In this schematic, superscripts \( a \) and \( b \) represent the edges of the square heater, \( Q \) is the heat flux, \( T_{\text{amb}} \) is the ambient temperature and \( T_{\text{hot}} \) is the temperature of the heater. \( Q_{\text{membrane}} \) represents the total heat flux through the heater membrane. (b) Heat flux versus air gap size between surfaces at 600 and 300 K (\( \Sigma = 1 \)); \( q \) is the variation of the conductive heat flux and \( d \) is the gap distance [52]. Curves 1 and 2 represent heat flux owing to conduction and radiation, respectively.

\( a \) is the thermal accommodation coefficient. As can be seen from this figure, the conductive heat flux increases fast for air gaps between \( 10^{-5} \) and \( 10^{-7} \) m and then approaches a high plateau as the air gap thickness decreases below \( 10^{-7} \) m. The plateau value results from the fact that heat conduction changes from a diffusive to a ballistic transport mechanism when the gap becomes extremely small. From this graph, it can also be appreciated that if the air gap is increased to a few
microns (see red dots)—a typical gap for surface micromachined structures—the heat loss owing to conduction is one order of magnitude lower than in the case of a nanogap.

(ii) Radiation

The radiative heat transfer between the two surfaces of the air gap, in theory, could be calculated from the Stefan–Boltzmann law,

\[ q_r = \varepsilon \sigma (T_1^4 - T_2^4), \]  

(3.6)

where \( q_r \) is the density of the radiative heat flux, \( \varepsilon \) is the emissivity and \( \sigma \) is the Stefan–Boltzmann constant. The radiative heat transfer between two surfaces as calculated from the Stefan–Boltzmann law does not take into account the size effect of the air gap \( d \) though. So when the gap distance \( d \) is of the order of or smaller than the maximum radiative wavelength at a specific temperature, the Stefan–Boltzmann expression must be amended as demonstrated by Whale & Cravalho [53]. The expression to use in that regime becomes

\[ Q_{12}(k) = \frac{hck^3}{4\pi^2 [\exp(hkc/\pi k_B T_1) - 1]} \left[ \frac{0.6806}{\pi^2 y^2} + \frac{m(m + 1)}{y^2} \right], \]  

(3.7)

\[ Q = \int_0^\infty [P_{12}(\omega) + P_{21}(\omega)]d\omega \]  

(3.8)

and

\[ y = \frac{kd}{\pi}. \]  

(3.9)

In these expressions, \( Q \) is the net radiative energy flux, \( h \) is Planck’s constant, \( c \) is the speed of light in a vacuum, \( k \) is the wavenumber, \( d \) is the air gap thickness, \( \omega \) is the angular frequency and \( m \) is the integer value of \( y \). The subscript 12 means the direction of heat flux is from surface 1 to surface 2, and vice versa. The gap distance in many MEMS structures is of the order where this amended Stefan–Boltzmann must be used rather than the Stefan–Boltzmann equation. From figure 9b, it can be concluded that the heat dissipation in air gaps by thermal radiation (curve 2) begins to play a very significant role when the gaps are in the range below \( 10^{-7} \) m. From the same curve, it is also obvious that heat loss by radiation from the hot sensor element becomes negligible when the air gap is in the micrometre range. Radiation losses can be reduced by coating the back side of the thin suspended membrane with a glossy material like gold. At the heater-radiated wavelengths, the best reflector materials are aluminium, silver, copper and gold. The four metals are approximately equal in reflecting infrared, while aluminium and silver are superior to the coloured metals in reflecting visible energy. Gold is preferred over aluminium for many reflector applications because of the variety of methods by which it can be applied to many substrate materials.

(iii) Convection

Air hardly flows in gaps of less than a dozen microns. The heat generated by the heater element is thus transferred to the substrate predominantly by heat conduction of air and thermal radiation between the surfaces. Consequently, it is usually assumed that there is no significant contribution of convectonal fluid motion because of the small size of the heated structures. The validity of this
assumption was supported by FEM simulations from Sberveglieri et al. [54] and Gotz et al. [55], who showed that the difference in simulated heat loss with or without convection is only about 5 per cent.

In the above treatise, we detail thermal losses owing to changes in the air gap thickness of the gas sensor. One must also consider lateral conduction heat losses from the suspended heater plate through the suspending arms connecting the heater membrane to the substrate (see figure 9a and four suspending beams connecting the heater membrane to the Si substrate in figure 8). Making the heater membrane thin and of low heat conductivity materials and making the suspending arms that hold the sensor membrane and act as electrical contact conduits very thin and narrow further minimize power losses. Finally, making the real estate occupied by the heater small in absolute size and small compared with the suspended membrane size further reduces the absolute power requirements [11]. We conclude that the total power consumption of miniaturized gas sensors can be minimized by:

— operating the heater at as low a temperature as possible;
— incorporating the heater element in a thin low thermal conductivity membrane;
— designing the heater as small as possible—a fraction of the area of the suspended membrane only;
— suspending the membrane heater elements at least a couple of micrometres above the substrate; and
— reducing radiation losses by coating the back side of the membrane with a glossy material like gold.

4. Integrating miniaturized heaters with nanomaterials for advanced gas sensing

In §§2 and 3, we reviewed progress towards better nanogas sensor materials and better micro- and nanogas sensor heater elements. We now look into how to combine these miniaturized heater and sensor materials in an optimum way in terms of gas sensitivity, lowest power budget and simplicity and cost of manufacture. In figure 10, we summarize the evolution of heater designs (column 1) and sensor materials (column 2) towards our recommended design shown at the bottom. For example, a microhotplate from column 1 could be combined with a porous thick film of MOS nanopowder particles (such as those described by Lee et al. [21]). The last entry in column 1 is that of a CNW heater element suspended between two carbon posts. The fabrication process of this nanoheater element is detailed in §5. The novel gas sensor we propose here combines a suspended CNW heater, shown in figure 11, with the optimum MOS material deposition method (bottom columns 1 and 2). Inspired by the gas sensor configuration in figure 4, where MOS nanoparticles are deposited on vanadium oxide nanobelts, we wanted to deposit MOS nanoparticles on CNWs. The big difference from the design in figure 4 is that the nanowire in our case is also a heater element suspended between two carbon-measuring electrode posts. As we came to understand from the current review, methods that are compatible with deposition of MOS nanoparticles on a nanowire include chemical methods with deposition from solution, as well as sol–gel techniques.
size reduction in heater (column 1) and particles of sensing material (column 2)

Figure 10. Effect of size reduction on materials and heaters of a gas sensor. In column 1, heater elements of a macro-Taguchi sensor, a microhotplate thin-film sensor and a suspended CNW sensor (see figures 7 and 8) are illustrated. Column 2 represents diagrams of polycrystalline sintered grains. The third picture in column 2 represents a proposed design for a nanogas sensor that uses a nanowire with a porous film of MOS nanopowder coated on it. Over the years, a combination of the most suitable heater from column 1 and material from column 2 would yield a sensitive and cost-effective nanogas sensor. (Online version in colour.)

Figure 11. SEM images displaying the diameter (a) and length (b) of a single suspended CNW. (c) Low-magnification SEM image displaying the adhesion of CNW onto C-MEMS electrode walls. (d) Carbon MEMS-CNW structure for gas sensing employing the suspended nanowire. (Online version in colour.)

and physical vapour deposition and CVD. An especially attractive approach to deposit an MOS locally on a brittle heater structure such as the CNWs in figure 11 is to use the heat of the heater element itself to initiate the CVD deposition from a metallo-organic precursor. As we already mentioned in §2, this approach for local CVD was pioneered by Cavicchi et al. [38].

Another more novel approach is to fabricate the MOS nanopowder together with the heater itself in a monolithic process described in §5. Importantly, the proposed suspended nanowire gas sensor, as shown in column 2 of figure 10, is a very simple one-port-type sensor (with only two contacts). In terms of electrical

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configuration, gas sensors are either one- (two contacts) or two-port-type (four contacts) devices [56]. Traditionally, MOS gas sensors are two-port sensors and have separate heater and sensing electrodes. In one-port gas sensors, the heater and sensor electrodes are the same and are used for both heating and measuring the changes in resistance that occur owing to the presence of detectable gases. The so-called pellistors or catalytic bead sensors [57] work this way. They consist of a fine powder of catalytic metals supported on an inert porous refractory ceramic coated onto a Pt wire that is used as both a heater and a sensor [58]. It is important to note that pellistors do not use any semiconductor material for sensing and therefore differ from a semistor (introduced below). In other words, pellistors measure the small changes in the conductance of the heater element (Pt wire) that results from the exothermic oxidation reactions taking place on the catalyst surface with the heater wire itself. In general, an MOS-based sensor is more sensitive and versatile since the sensitivity of a pellistor or semistor is based on temperature change; however, catalytic-type sensors exhibit more linear and reproducible characteristics [59].

A combination of an MOS-based gas sensor with the one-port operating mechanism used in a pellistor was proposed by Williams & Coles [58], who called this new device a semistor (i.e. a semiconductor-based pellistor). A semistor is prepared by coating a sensitive low-resistance MOS such as SnO2 directly onto a Pt wire coil. A semistor exploits the sensitivity and resistance modulation capabilities of an MOS material while maintaining the linearity in behaviour and ease of manufacture of a pellistor. The nanowire gas sensor we propose is of the semistor type where resistance changes in the MOS are caused by both heat of reaction and injection and extraction of electrons. Given the challenge of patterning two measuring electrodes on an MOS porous film covering a CNW, the semistor approach is probably the only practical way to develop nanowire-based gas sensors. Recently, Bissi et al. [60], the same group that introduced the ultra-low-power microhotplate that ran at an unprecedented low-power value of 8.9 mW (see above), switched to a semistor-like approach. These investigators do introduce a novel three-terminal device by patterning a single metallization layer (Pt) and, as in a semistor approach, there is no passivation layer for electrically insulating the sensing layer from the heater in their design. This resulted in a simplified, cost-reducing fabrication process that came with even lower power consumption. Their three-terminal sensor features a two-contact circular heater and a single measuring electrode. The role of the heater is twofold: when biased with a suitable voltage, it maintains the sensor at the correct operating temperature and at the same time it acts as the second electrode for contacting the sensing layer. When a known voltage difference is applied between the heater and the third electrode, the current leaking from the heater through the sensing layer is acquired. This three-terminal approach might be possible to implement in our proposed suspended nanowire gas sensor as there is no need for patterning of the third electrode in this case.

5. Proposed fabrication of suspended CNW gas sensors

In our laboratory, we have designed a novel suspended CNW-based gas sensor. These CNWs are composed of glassy and graphitic carbons and display very
high temperature resistance. This material is very suitable as a miniaturized heater in a gas sensor owing to the structural stability of carbon at very high temperatures. The fabrication of these wires involves heating at 900°C and therefore no further testing for thermal stability is required up to this temperature. The thus fabricated sensors may have one or many suspended CNWs connected to carbon microelectrodes without any glue or clip. These nanowires have an aspect ratio as high as 1000 with sub-50 nm diameters and approximately 30 μm lengths. The resistance value of these wires falls between that of glassy carbon and graphite. Structural characterization using X-ray diffraction, Raman analysis and high-resolution transmission electron microscopy imaging confirmed that these nanowires contain both amorphous and crystalline carbon regions.

These suspended CNWs are deposited by electrospinning of a polymer precursor on MEMS support structures. The MEMS support structures are fabricated by employing standard SU-8 photolithography and the support structure and suspended polymer nanofibres are carbonized together at 900°C in a non-oxidizing environment. The details of this C-MEMS/C-NEMS fabrication process can be found in Sharma et al. [61]. Electrospinning is one of the simplest and least expensive techniques for the fabrication of ultrathin polymer fibres. In the past several decades, different types of organic polymers and inks have been successfully processed as nanofibres using this technique, with typical examples including various biopolymers, electrically conductive polymers and fluorescent polymers. Recently, our group was able to modify the electrospinning technique to put polymer nanofibres down in an extremely controlled fashion on both flat and three-dimensional structured surfaces [62]. As a result, after pyrolysis, we can now produce CNWs of precise length and position on an appropriate high-temperature substrate. The resulting carbonized structure also comes with integrated contact pads, and we demonstrated ohmic contact between the carbon wire and the support structures. In a typical design, the contact pads are 0.5 × 0.5 cm and are connected to two SU-8 supporting walls that are 20 μm wide with a 20 μm gap in between. The gap between the two walls supporting the CNWs becomes approximately 30 μm as the walls shrink during pyrolysis. The structures are fabricated on a Si substrate that is coated with an insulating layer of thermal SiO₂ to ensure insulation for electrical characterization of the carbonized fibres and the C-MEMS-supporting structure and contact pads.

Typical SEM images of single suspended CNWs are shown in figure 11a–c. In figure 11a,b, a 42.22 nm thick nanowire with a length of approximately 29 μm is shown. It can be observed that the CNWs have a very uniform geometry. However, to account for any experimental or imaging error in determining the diameter of CNWs, SEM pictures were taken at three or four different points along the length of the wire. Uniformity of the wires to within 10 per cent was observed. In figure 11c, a lower magnification SEM image illustrates the adhesion of a typical CNW onto the carbon walls. The walls are further connected to 0.5 mm wide electrode pads that can be conveniently connected to an external power supply to yield a gas sensor like the one shown in figure 10 (column 2, row 3: a combination of CNW with nanopowder).

For nanogas-sensing applications, the CNWs shown in figure 11 are used as extremely low-cost, low-power heater elements. In §§3 and 4, we detailed various MOS deposition techniques and singled out local CVD as a most appropriate
method to deposit nanopowders on the CNW. These CNWs can be locally heated by applying a current and, since the resistance of the wire is much higher than the rest of the structure (such as the nanowire-supporting electrodes), MOS nanocrystals only deposit on the nanowire and not on the support structure. As discussed above, to keep the sensor structure as simple as possible, no separate measuring electrodes are applied over the MOS nanocrystal film on top of the carbon nanoheater; instead, the gas sensor is operated as a one-port nano-semistor where heat changes and electron injection or extraction owing to reactions result in MOS resistance changes that are measured on the CNW itself. In a slightly more complex process, we could attempt a three-terminal device, as described by Bissi et al. [60], and deposit a third sensing electrode on the outside of the nanoporous film.

Besides using the heat of the nanowire heater to locally deposit all types of MOS nanocrystals directly onto the nanoheater, we are experimenting with another less conventional approach towards integrating MOSs on the CNWs. In this alternative approach, we rely on the preparation of mixtures of nanopowders in a polymer solution that can be electrospun. After electrospinning, the entire structure (integrated nanopowder–nanowire–supporting MEMS structure) is then pyrolyzed together. Along this line, we have already fabricated composite PAN/CNT [63] nanofibres. The right concentration of the MOS nanopowder is expected to lead to hybrid MOS–CNWs suspended on carbon microwalls, which are in turn connected to carbon macroelectrodes.

6. Conclusion

The evolution in gas-sensitive materials and heater structures for MOS gas sensors from macro- to nanosize was reviewed. Size reduction of the grains in an MOS gas-sensitive material leads to lower operating temperatures, lower LOD, higher sensitivity, faster response time and less reliance on expensive metal catalysts. Size reduction of heater elements in turn leads to a lower overall power budget, faster heating and cooling, lower propensity for cracking under heat stress and mass production amenable to manufacturing techniques. The objective of this review was to suggest better ways to combine progress in these two areas so as to enable better gas sensors for the future. In this context, we are suggesting optimal combinations of nanomaterial deposition methods (e.g. local CVD of MOS nanocrystalline films directly on the heater) with optimal fabrication techniques for the lowest power budget nanoheaters (e.g. a C-NEMS suspended nanowire heater). A futuristic device we are researching to illustrate this combination is a nano-semistor. This is a simple one-port gas sensor based on a suspended CNW made using C-NEMS and C-MEMS coated with nanocrystalline MOSs. The carbon wire in this nanogas sensor is both the heater and the sensing element. The authors believe that this device will offer all the sensing advantages one expects from an optimal combination of nanoheater construction and optimized nanocrystalline gas-sensing material deposition.

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