Co-doped ZnO Nanowires for Low Temperature Methane Sensing Operational in Humid Environments

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Highlights

- ZnO nanowire films were demonstrated for chemiresistive sensing of methane.
- Co-doping of the ZnO nanowires resulted in a reduced operating temperature and enhanced sensitivity and selectivity towards methane.
- The improvement in sensor performance upon Co-doping was attributed to increased numbers of active sites for oxygen adsorption.
- A drop-cast molecular sieve layer was shown to reduce relative humidity effects at the metal-oxide nanowire surface to allow for methane detection in humid environments.

1. Introduction

Methane (CH_4) is a common greenhouse gas that has been studied for hundreds of years since its discovery in 1778. Recently methane has achieved great prominence in the public domain because of its more significant role than carbon dioxide in the greenhouse effect [1]. Monitoring the presence and concentration of methane is a major safety issue for a number of industries (limit of explosion = 5% or 50,000 ppm) [2]; for example, in coalmines, power plants, waste water treatment, landfill sites and the petroleum chemical industry [3, 4]. From a biomedical application perspective, methane is one of a set of biomarkers related to gut metabolism [5]. As methane has low solubility in blood, it is rapidly excreted by the lungs and can be monitored in breath [6] and also emanates from skin [7, 8]. In the body, methane is derived from colonic anaerobic bacterial fermentation of carbohydrates in the large intestine associated with intestinal disease [9]. Thus, there is a broad range of needs for monitoring methane across environmental, industrial and biomedical settings where sensing requirements (e.g. selectivity, sensitivity, etc.) are diverse.

Current approaches to methane sensing include the use of infrared imaging [10], electrochemical and optical sensing [11, 12], and mass spectrometry techniques such as selected ion flow tube mass spectrometry (SIFT-MS) [13] and gas chromatography-mass spectrometry (GC-MS) [14]. For example, Wang et al. [15] explored computer vision approaches for infrared imaging of methane based on convolutional neural networks to determine methane leakage, aiming for automatic leak detection. Sekhar et al. [16] reported an electrochemical metal oxide methane sensor using Sn-doped indium oxide which exhibited responses above 100 ppm CH_4 . This mixed potential sensor was applied in the detection of unburnt methane in natural gas. Allsop et al. [17] studied the wavelength shift in a multi-layered structure of Pt-ZnO in the presence of CH_4 exhibiting a volume limit of detection of

2% (20,000 ppm) methane resulting in the possibility of optical sensing of CH₄ to cater for safety concerns. In terms of biomedical applications, CH₄ levels in breath can be measured using the commercial BreathTracker Analyzer (Quintron Instruments). This instrument separates breath components by the basic principle of GC, using room air as the carrier gas. After separation from other components, the methane is then detected using a solid state sensor [18]. This device exhibits a linear range of 2-75 ppm for CH₄ and a resolution of 1 ppm. Shortcomings of the BreathTracker Analyser include a long pre-heating time (>8 h) and complexity in terms of calibration and sampling by manual injection. Other GC based approaches have also been used to analyse CH₄ in breath [19]. Gao et al. [20] for example designed a miniaturized Fast GC system using a metal oxide sensor as detector to simultaneously quantify hydrogen and methane in breath over the range of 2–200 ppm. GC based systems often use drierite dessicant saturated with cobalt chloride to remove water vapour from breath samples prior to analysis.

The use of chemiresistive gas sensors based on metal oxides remains the most common robust approach for gas sensing in general for environmental and industrial applications owing to their low cost, high sensitivity to a range of gases, operating speed, small size and relative simplicity [21]. However, CH₄ is more challenging than other gases to detect particularly at low concentrations, due to its non-polar nature and the high enthalpy of the C–H bond [22]. The metal oxide gas response (n-type such as ZnO, SnO₂ and p-type such as CuO and Cr₂O₃) can be tailored in a number of ways in order to modulate selectivity and sensitivity via morphology tuning and chemical modification [23], e.g. by the surface modification [24, 25] or solution based doping [26, 27] to incorporate suitable additives such as noble metals [28]. ZnO for example has a diverse number of growth morphology types, can be synthesised easily, and has a high electron mobility and thermal conductivity, as well as a wide and direct band gap making it suitable for a wide range of sensing applications [29]. By employing electrochemically grown

ZnO thin films for example, Basu et al. [30] achieved a response of 4.82 ± 2 ($\Delta R/R$) to 1% (10,000 ppm) methane at an operation temperature of 220°C. Ponzoni et al. [31] reported the detection of a lower concentration of CH₄ (50 ppm) with ZnO nanoparticle films without any catalyst, additives or buffer layers. However, a high temperature of 500°C was required. This ZnO nanoparticle-based sensor was developed to address food quality control as well as the detection of microbial metabolites in human sweat. The sensor was part of an array that was integrated with a humidity compensator to maintain a constant humidity level throughout the testing process. The development of a low-temperature metal oxide-based sensor for low concentration methane sensing (<100 ppm) remains an active research goal. To the best of our knowledge, there are only few reports on low concentration methane sensing (<100 ppm) using ZnO at low temperatures [32]. Hu et al. [33] recently reported methane sensing using Co-doped ZnO microstructures at a concentration of 50 ppb. This analysis was carried out at 140°C. However, no humidity testing was carried out on this sensor which is important for applications such as in the breath matrix.

The objective of this research was to develop a low temperature ZnO nanowire (NW)-based chemiresistive sensor capable of the selective detection of CH₄ in the analytical range relevant to breath (1-100 ppm) [18]. We employed a hydrothermal method for the preparation of ZnO NWs and explored the effect of doping this material with Co on methane sensing. The effect of operating temperature and concentration of Co used as dopant were explored and a gas sensing mechanism is proposed. Finally, given that the response of metal oxides is well-known to deteriorate in humid conditions, it was assessed if humidity could be mitigated by the modification of the ZnO NW film by way of a molecular sieve coating. Overall, we demonstrate the potential that Co-doped ZnO NWs have for CH₄ detection. Given the low operating temperatures employed, the high selectivity for methane and the initial demonstration

of the mitigation of humidity, this work shows this material's particular relevance to methane detection for biomedical applications such as in breath.

2. Materials and Methods

2.1 ZnO nanowire growth

ZnO NW growth was carried out using a hydrothermal method. The first step was to synthesise ZnO nanoparticles to be used as a seed layer for the growth of NWs from substrate. ZnO nanoparticles were prepared using a chemical route (described elsewhere [34]) wherein, 50 ml of 30 mM NaOH solution in ethanol was added drop wise to 25 mL of 10 mM zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$, in ethanol at 70°C under continuous stirring for 2 h (volume ratio of the two solutions was maintained at 2:1). The resulting nanoparticles solution was stable for a period of up to 2 weeks. These were coated onto $8 \times 10 \text{ mm}^2$ n-type <100> Si substrates (coated with 120 nm SiO_2 layer, Inseto UK Ltd.) by spin-coating (3 times) followed by a drying time of 10 min at 90°C. Coated substrates were suspended face down in an equimolar aqueous solution of zinc nitrate hexahydrate, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (25 mM), and hexamethylenetetramine (HMTA), $(\text{CH}_2)_6\text{N}_4$ (25 mM) at 90°C for 6-8 h in a beaker covered with Petri dish to minimise evaporation. ZnO NWs growth was completed after removal of substrate from the beaker, rinsing thoroughly using de-ionized water and drying under Ar flow.

2.2 Modification of ZnO nanowires with Co

Co-doped ZnO NWs were prepared by adding Co^{2+} in the aqueous solution used for NWs hydrothermal growth from the ZnO nanoparticle seed layer. In a beaker (50 mL), a specified concentration of cobalt acetate tetrahydrate, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (5, 10, 20 mM) was mixed with equimolar solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{CH}_2)_6\text{N}_4$ and hydrothermal growth was

initiated as described in Section 2.1. Hereafter, these samples are referred to as Co(d):ZnO NW films, where d is the concentration (mM) of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ used during hydrothermal synthesis.

2.3 Gas sensing

Gas sensing measurements were carried out using a two-point probe configuration after sputter deposition of two gold electrodes (120 nm thick with spacing 0.1 mm, attained using a mask) on top of the ZnO NW films. The gold electrode-deposited ZnO NW films were mounted on an alumina base and fixed with two Pt-100 heaters (RS Radionics, Dublin) to maintain and control the operating temperature of the sensor. The response of the sensor to various gases (CH_4 , NH_3 , H_2 , $\text{C}_2\text{H}_5\text{OH}$) in ambient conditions was recorded using a static gas sensing set-up (Fig. S1). An air bubbler and a humidity sensor (Sens Humid/Temp 5 V analog $\pm 3\%$ accuracy, Digi-key) were incorporated in the set-up for sensing measurements at various relative humidity values (RH). The sensor was mounted in an enclosed glass chamber (100 cm^3) and the required concentration of test gas in the chamber was attained by introducing a measured quantity of gas using a syringe. Response curves were measured by applying a fixed bias of 2 V across the gold electrodes and the time dependence of resistance was recorded using a Labview-based data acquisition system. After attainment of steady state, recovery of the sensors was recorded by exposing them to ambient. The sensitivity (S) was calculated from the response curves using the equation:

$$S (\%) = (R_a - R_g)/R_g \times 100 \quad (1)$$

where R_a and R_g are the resistance values of the sensor in ambient and in the presence of test gas, respectively.

2.4 Characterisation of the ZnO NW films

Surface morphology of the ZnO NW films was investigated using scanning electron microscope (SEM) (Hitachi Model: S3400N). Electrochemical impedance spectroscopy (EIS) measurements were performed on the gold electrode coated ZnO NW films using a CHI660C electrochemical workstation over a frequency range of 0.1 Hz to 1 MHz, applying an AC signal of 10 mV in amplitude.

2.5 ZnO NW film modification with a molecular sieve

Firstly, 60 mg of a meso-porous silica molecular sieve powder (SBA-15, Sigma-Aldrich, 777242) was mixed with 1 mL ethanol and ultrasonicated to form a homogeneous slurry. Ethanol is a commonly used cosolvent for SBA-15, which can function as swelling agent resulting in the formation of large pores [35]. The molecular sieve was then coated onto the ZnO NW and Co(10):ZnO NW films using a dip-coating method, followed by a heat treatment at 200°C to render the SBA-15 film stable. This was followed by sputter-deposition of gold electrodes. Hereafter, SBA-15 coated samples are referred as ZnO(SBA-15) NW and Co(10):ZnO(SBA-15) NW films. Both ZnO(SBA-15) and Co(10):ZnO(SBA-15) NW films were exposed to CH₄ gas (20 ppm) in the presence of controlled levels of RH (%), and their chemiresistive responses were compared.

3. Results and discussion

3.1 Sample characterisation

The hydrothermal method of NW synthesis was used for this work as it provides a facile route to obtaining dense uniform NW growth over large substrate surface areas, which is required for gas sensing. NW films (pure ZnO and Co-doped NWs) were prepared for this study as described in Section 2.1 and the NW morphologies imaged using SEM (Fig. 1). Fig. 1 (a) &

(b) show top-view images of as-grown pure ZnO NW and Co(10):ZnO NW films. It can be observed in Fig. 1(a) that the as-grown NWs form a dense inter-connected random network having variable NW diameters (100-200 nm) and orientation attributed to the random distribution of the initial ZnO nanoparticle seed layer on the Si/SiO₂ substrate. Fig. 1(c) depicts the quasi-hexagonal facets in Co(10):ZnO NWs indicating preferentially oriented growth along c-axis, which is in accordance with the growth habit of wurtzite crystals [36]. An increase in diameter (~500 nm) of ZnO NWs was observed after Co inclusion due to its interference with the nucleation process. This can be explained as during the hydrothermal synthesis, Co²⁺ compete with Zn²⁺ in forming complexes with hydroxide ions, reducing the interaction between Zn²⁺ and OH⁻ ions and altering the overall nucleation process. This competing mechanism can promote lateral growth rather than perpendicular growth [37] and as a result, the diameter of the NWs in the resulting film increases. It is noteworthy to mention that the growth of NWs onto Si/SiO₂ substrate is highly reproducible under controlled temperature and precursor solution concentration conditions. Modification of NWs with Co is facile and reproducible, thereby making the film fabrication process highly amenable to sensor fabrication.

Fig.1. SEM images of (a) as-grown pure ZnO NWs, (b) Co(10):ZnO NWs and (c) high resolution image of hexagonal facets in Co(10):ZnO NWs.

To electrically characterise the effect of Co-doping in ZnO NWs, impedance measurements were carried out on films of pure ZnO NWs, Co(10):ZnO NWs and Co(20):ZnO NWs. Charge carriers moving through the films must overcome the resistance of the bulk NW material, the grain boundaries between NW junctions, and the dielectric properties of the NW-electrode interface. The impedance data generated for these films (Fig. 2), presented in the form of Nyquist plots exhibit a single semi-circle having a non-zero x-intercept for each of the three films, ZnO, Co(10):ZnO and Co(20):ZnO NWs. Similar behaviours are observed for ZnO nanostructures elsewhere [38, 39].

Fig. 2. (a) Nyquist plots of ZnO, Co(10):ZnO and Co(20):ZnO NW films (equivalent circuit model in inset).

The impedance spectra obtained were fitted to an equivalent circuit model ($R_b(R_j||C_j)$), in order to extract out the different electrical parameters (Table 1), where R_b is the resistance of the bulk NWs, and R_j and C_j represent the resistance and capacitance of the NW junctions, respectively. In the Nyquist plot, the high-frequency x-axis intercept is taken as R_b . The single semi-circle may be attributed to the relaxation frequency of the electrical processes through the NW junctions. It may be that the NW-electrode interface has a similar relaxation frequency to that of the NW junctions, explaining why this process does not result in a distinct semi-circle [40]. Alternatively, it could also be that the time constant for the NW-electrode interface is very small, thus yielding a large relaxation frequency beyond our measurement range.

Table 1. Parameters obtained from fitting the impedance spectra for the different films to the proposed equivalent circuit model $R_b(R_j||C_j)$.

	R_b (Ω)	R_j (Ω)	C_j (pF)
ZnO NWs	2405	160220	2.552E-11
Co(10):ZnO NWs	41.35	14481	4.167E-9

Co(20):ZnO NWs	22.63	13195	4.058E-9
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It is evident that the modification of ZnO NWs with Co resulted in a decrease in the overall resistance and capacitive nature of the ZnO NW films (Table 1). This is in agreement with the SEM images (Fig. 1) where it was observed that Co-doping led to higher crystallinity and an increase in grain size. This increase in grain size likely reduces the scattering of the charge carriers by grain boundaries, and thus decreases R_j and C_j with increasing Co concentration used.

It should also be noted that bonding of oxygen with the Co^{2+} ions in tetrahedral symmetry is weaker than that of oxygen with Zn^{2+} ions in ZnO, and hence the bonding strength of oxygen becomes weaker near Co^{2+} ions as compared to the host ions (Zn^{2+}) in the lattice [41]. This may result in enhancing the donor-type vacancies with Co dopants. The decrease in R_b with increasing Co content may be indicative of the generation of carriers by donor-type vacancies and these are relatively weakly bound to the defects (oxygen vacancies). Similar results have also been observed [42] in Co-doped ZnO nanopowders, where it was shown that the concentration of oxygen-related defects increased with increasing amounts of Co dopant.

3.2 Gas sensing studies

In order to assess the CH_4 sensing properties of ZnO and Co(d):ZnO NW films, Co(d):ZnO NW films ($d = 5, 10, 20$) were exposed to CH_4 (50 ppm). In the first instance, the operating temperature was held at 50°C and the sensor response (S (%)) was monitored as a function of d , where d refers to the concentration of Co salt used in the hydrothermal growth synthesis (Fig. 3(a)). It can be observed that maximum sensitivity (7.7% at 50°C) was obtained for $d = 10$ for all temperatures apart from the highest temperature investigated (240°C). Therefore,

Co(10):ZnO NW films were selected for further investigation of the gas sensing properties of Co-doped ZnO NW films.

Fig. 3. (a) Sensitivity to methane (50 ppm) as a function of d (concentration of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ used in the ZnO NW hydrothermal synthesis); operating temperature 50°C; and (b) S (%) and R_a as a function of operating temperature for ZnO and Co(10):ZnO NW films.

In order to establish the optimal operating temperature, S (%) was measured as a function of temperature (RT – 240°C) for both ZnO and Co(10):ZnO NW films (Fig. 3(b)). It also depicts the variation of R_a as a function of temperature for both ZnO and Co(10):ZnO NW films. It can be seen that the Co(10):ZnO NW films exhibit greater sensitivity to methane for operating temperatures up to 200°C compared to pure ZnO NWs. Also, a lower optimal operating temperature of 50°C is achieved as a result of Co-doping compared to un-doped ZnO NW films which exhibited a maximum sensitivity at 150°C. Note that testing at 37°C was carried out to explore the compatibility of sensor operation at body temperature. Although responses were obtained at this temperature, sensitivity was optimal at 50°C and therefore all further experiments were carried out at this higher temperature. From this data, it can be concluded that optimised levels of Co-doping of ZnO NWs improves sensitivity towards CH_4 as well as reduces the optimal operating temperature (from 150°C to 50°C). This has several advantages – lower operating temperatures result in lower power consumption and in terms of health

applications, operating temperatures near body temperature, could allow for future on-body sensing applications for monitoring methane emissions from the body.

A selectivity study was carried out to investigate the cross-sensitivity of the ZnO NW films to other gases. NH_3 , $\text{C}_2\text{H}_5\text{OH}$ and H_2 gas were selected on the basis that they are components of the breath volatile emission. In addition, these analytes are reported in the literature as generating chemiresistive responses from ZnO-based sensors [43–45].

Fig. 4. Selectivity histogram for ZnO and Co(10):ZnO NW films for gases (20 ppm) measured at 150°C and 50°C, respectively.

The responses upon exposure of the different gases (20 ppm) to ZnO NWs (operating temperature: 150°C) and Co(10):ZnO NWs (operating temperature: 50°C) were monitored and selectivity histogram is given in Fig. 4. Both films exhibited responses to all gases tested except for ethanol. However, it is evident that the Co(10):ZnO NW films were more selective towards CH_4 than pure ZnO NWs as they exhibit a 5 times higher sensitivity towards CH_4 and a similar or lower response to the other gases. Table 2 gives the selectivity coefficients for each film for each gas relevant to their response to CH_4 and it can be seen that Co-doping in ZnO NWs improved selectivity towards CH_4 . This shows how properties of a metal oxide-based film,

ZnO NWs in this case, can be controlled by tuning conditions to render them specific towards the gas analyte of interest.

Table 2. Selectivity coefficient values for pure ZnO and Co(10): ZnO NWs for CH₄ relative to other specified gases. Values calculated according to formula: Selectivity Coefficient= S_{gas}/S_{CH_4} . Gas concentration: 20 ppm.

Selectivity Coefficient		
Gas	<i>ZnO NW film</i>	<i>Co(10):ZnO NW film</i>
CH₄	1	1
NH₃	0.28	0.12
C₂H₅OH	0	0
H₂	0.17	0.05

To further understand the interaction of CH₄ with the sensing films, response curves were generated showing the resistance changes of the films (ZnO and Co(10):ZnO NWs) for increasing concentrations of CH₄ (Fig. 5 (a)&(b)).

Fig. 5. Response curves as a function of time exposure for increasing concentrations of CH₄ to (a) pure ZnO NW films at 150°C, and (b) Co(10):ZnO NW films at 50°C. (c) Calibration curves generated from data in (a) and (b).

The decrease in resistance of the ZnO NW films (Fig. 5(a)) upon CH₄ exposure is attributed to the quenching of chemisorbed oxygen ion species on the surface, restoring electrons into the ZnO conduction band (see Section 3.3). Co(10):ZnO NW films exhibited a similar trend in resistance change (Fig. 5(b)). The response curves demonstrate that both types of film underwent resistance changes upon exposure to CH₄ which was observed to increase with gas concentration. Typical response and recovery times (defined as the times needed for 90% of total change in resistance on exposure to test gas and ambient air, respectively) measured for ZnO and Co(10):ZnO NW films upon exposure to CH₄ (10 ppm) were 33 s and 50 s; and 52 s and 75 s, respectively. The faster response of pure ZnO NW films is attributed to the higher

operating temperature. It is evident that the Co(10):ZnO NW films exhibit an enhanced response to CH₄ compared to that of ZnO NW films over the concentration range investigated.

To explicitly compare the responses of the films, *S* was plotted as a function of CH₄ concentration in Fig. 5(c). The lowest concentration of methane detected by pure ZnO NW films was 5 ppm at 150°C, while a concentration of 1 ppm was reached for the Co(10):ZnO NW films operating at 50°C. For CH₄ levels above these values, all samples exhibited linearly increasing sensitivity up to 100 ppm with maximum sensitivity values of 3.2% and 11.6% for pure ZnO and Co(10):ZnO NW films, respectively. These results clearly suggest that doping ZnO NWs with Co using an optimised concentration of 10 mM Co(CH₃COO)₂·4H₂O, resulted in an enhanced sensing performance towards CH₄ at a low operating temperature.

In addition to enhanced sensitivity values and lower operating temperatures, the stability and reproducibility of a sensor is also critical for reliable device development. Fig. 6 shows data for a stability study performed on Co(10 mM):ZnO NW films over a period of 20 days, wherein the resistance of the sensor in ambient (*R_a*) and in presence of methane (10 ppm) (*R_g*), was taken daily. It can be seen that both *R_a* and *R_g* were stable over 20 days. A low concentration of CH₄ was used for the stability study to ensure that the sensor response in ambient and in methane could be discriminated even at this low gas concentration. A t-test was also performed to support that *R_a* and *R_g* were significantly different at the 95% confidence level (*p* < 0.05).

Fig. 6. Resistance measurements of Co(10 mM):ZnO NW films in ambient (black dots) and in presence of 10 ppm CH₄ (red dots), sampling daily over a period of 20 days. Solid lines represent average resistance values and dotted lines represent the corresponding 95% confidence intervals.

3.3 Gas sensing mechanism

In ambient conditions, atmospheric oxygen is chemisorbed on the surface of the polycrystalline ZnO semiconductor which consists of large numbers of grains and grain boundaries that provide active surfaces for the adsorption of oxygen species. Oxygen is adsorbed on the ZnO surface in different forms depending on temperature, usually from physisorption ($O_{2(\text{phys})}$) to chemisorption($O_{2(\text{chem})}$) as shown below (Eq. 2) [46], which alters the local potential barriers between the grains and affects the electrical properties of the surface.

The species, $O_{2(\text{phys})}$, $O_{2^-(\text{chem})}$, $O^-(\text{chem})$ and $O^{2-}(\text{chem})$ exist at temperatures ~ 200 K, from room temperature (298 K) to $\sim 150^\circ\text{C}$ (423 K), from 150°C (423 K) to 400°C (673 K) and above 400°C (673 K), respectively [47]. These oxygen ions are formed due to trapping of electrons by molecular oxygen from the conduction band of ZnO. Fig. 7(a) shows a schematic of the band diagram depicting oxygen surface adsorption on pure ZnO NWs. The flow of e^- from bulk ZnO into the chemisorbed O^- layer induces a space charge between the interior of the

semiconductor and its surface. This negative surface charge is compensated by formation of a space-charge layer due to an accumulation of holes, leading to the formation of a depletion region. The energy band at the surface bends upwards with respect to the Fermi level.

Fig. 7. (a) Energy band diagram for pure ZnO depicting oxygen adsorption on its surface, (b) modified energy band diagram of ZnO depicting increase in defect levels and shifting of bands due to Co-doping, (c) schematic showing interaction of CH_4 gas molecules with adsorbed oxygen on the surface of a pure ZnO NW, and (d) schematic showing enhanced interaction of CH_4 gas molecules on the surface of Co-doped ZnO NW surface.

Co-doping is reported to improve surface states by enhancing the number of defect levels in ZnO, both in Zn interstitials and oxygen vacancies [48, 49]. Fig. 7(b) depicts the changes in

the energy bands of ZnO upon Co doping. As discussed in Section 3.1, Co-doping results in an enhancement of donor type vacancies effectively undergoing hybridisation with the intrinsic donor type oxygen vacancies and Zn interstitials [50]. As illustrated, dense defect levels in Co-doped ZnO NWs increase the availability of free charge carriers in the conduction band leading to enhancements in oxygen adsorption, e.g. as O_2^- species at temperatures $\sim 150^\circ\text{C}$, and lowering of band bending accompanied with reduction in depletion region depth. This resulted in the reduction of baseline resistance in Co-doped ZnO by an order of magnitude (Fig. 2). These dense defect levels are thought to occur in the case of the Co(10):ZnO NWs, that have increased active sites to assist in enhanced interaction with CH_4 gas molecules, as compared to its pure counterpart.

A schematic of the ZnO NW surface is presented in Fig. 7(c) wherein CH_4 molecules can interact with the chemisorbed oxygen layer, releasing electrons into the bulk of the host matrix according to the reaction:

where $\alpha=1, \beta=1$ at 150°C ; $\alpha=2, \beta=1$ at 50°C

This is likely what leads to the decrease of resistance upon CH_4 exposure for pure ZnO NWs at the operating temperature of 150°C (Fig. 5(a)). The same scenario is shown for the Co-doped ZnO NW surface in Fig. 7(d), this time at an operating temperature of 50°C wherein an increased amount of adsorbed oxygen species (O_2^-) is available for interaction with CH_4 . Thus, on exposure to CH_4 , there is a release of e^- into the Co(10):ZnO NW host matrix resulting in the observed decrease in resistance (Fig 5(b)), a similar trend to that observed for pure ZnO NWs. However, Co-doping yielded better gas sensing properties by increasing sensitivity and reducing the operating temperatures on account of increased active sites facilitating enhanced interaction with methane gas molecules.

3.4 Effect of Humidity

Moisture is one of the crucial influencing factors that must be considered with respect to the practical use of metal oxide sensors, as their response is easily influenced by relative humidity (RH) conditions. Depending on the application, RH may be important to consider as a potential interferent. RH for example is a major component of breath (80-90 %) [51] and as such can interfere with the detection of gas species when using metal oxides. To mitigate the effect of moisture on the sensing properties of the metal oxide films, a moisture filter layer comprising SBA-15 molecular sieve was coated directly onto the pure ZnO and Co(10):ZnO NW films (see Section 2.4) and are referred to here as ZnO(SBA-15) and Co(10):ZnO(SBA-15) NW films, respectively. SBA-15 is a mesoporous silica molecular sieve with a regular pore channel from top to bottom. The pore diameter (9 nm) is significantly larger than the diameter of a CH₄ (0.380 nm), allowing CH₄ to diffuse through it. SBA-15 has previously been composited with metal oxide materials for humidity sensing [52, 53] where exposure to moisture leads to hydrolysis of the surface siloxane bonds (Si–O–Si) yielding silicon hydroxyl bonds (Si–OH). In a dry environment, this process can reverse, as the silicon hydroxyl bonds can condense back to siloxane bonds [54]. Liu et al. [55] used SBA-15 as an effective moisture filter layer on top of a Pt-SnO₂ core-shell nanowire film for acetone sensing and the sensors were tested in the range of 25-100% RH. SBA-15 coated films exhibited a sensitivity decay of ~7% towards acetone when operated at 100% RH.

In order to understand the effect of RH on the ZnO NW sensors in this study, the resistance of the films was recorded at various RH values (25-85%), where 25% corresponds to ambient conditions. The data for pure ZnO and Co(10):ZnO NWs are shown in Fig. 8(a)&(b), respectively. Both sensors exhibited a decrease in resistance with increasing RH which may be attributed to an induced ionic conduction along the adsorbed water molecules [56]. Water

molecules approaching the ZnO NW surface become chemisorbed on the surface at lower RH and further physisorption occurs at higher RH. Conduction in the chemically adsorbed water monolayer occurs through the hopping of H^+ along the water layer. As RH increases, layers of water molecules are adsorbed physically onto the chemically adsorbed layer, binding to the hydroxyl group (OH^-) and generating H_3O^+ , which then becomes the dominant charge carrier. As RH continues to increase, water molecules occupy the inter-particle voids forming bridges between grain boundaries assisting ionic conduction through both H^+ and H_3O^+ hopping [57]. Similar trends were seen for the ZnO and Co(10):ZnO NW films where, in the presence of the SBA-15 coating, the resistance at ambient conditions is higher while the magnitude of decrease in resistance values over the RH range is reduced.

Fig. 8. Background resistance as a function of RH (%) for bare and SBA-15 coated (a) ZnO NW, and (b) Co(10):ZnO NW films. Sensor response (S(%)) to 20 ppm of CH₄ as a function of RH (%) for bare and SBA-15 coated (c) ZnO NWs and (d) Co(10):ZnO NWs sensor films. Operating temperature: 50°C.

In humid conditions, H₂O molecules will compete with oxygen for surface sites, limiting oxygen adsorption. Thus, with increasing RH, the number of reactive sites available for CH₄ oxidation reduces, resulting in a lowering of the sensor response (S). The sensor response to CH₄ (20 ppm) is shown in Fig. 8(c)&(d) for the pure ZnO and Co-doped ZnO films respectively. The efficacy of the SBA-15 layer is evident again in relation to S whereby the decrease in sensitivity is much lower across the RH range investigated for SBA-15 coated films compared with the bare films. For example, for pure ZnO films (Fig. 8(c)), the decay in response going from 25% to 85% RH is ~55% without SBA-15 which reduced to ~20% in the presence of the SBA-15 coating. The results are similar for the Co-doped films (Fig. 8(d)) where the sensor response at 85% RH was ~51% without SBA-15 and ~18% with SBA-15. This data clearly establishes that the SBA-15 molecular sieve layer can reduce the decay in sensitivity expected at high RH conditions for these methane sensors. On account of the incorporation of the molecular sieve to mitigate the effect of humidity, the Co(10):ZnO(SBA-15) NW films could represent a promising candidate for methane breath sensing.

4. Conclusion

We have synthesized Co-doped ZnO NWs by a hydrothermal process promoting ZnO NW growth. It was found that the Co-doped NWs synthesised with an optimised concentration of Co salt (10 mM), yield NW-based films that operated at an optimally low temperature of 50°C and were highly selective to methane. The lowest measured concentration of CH₄ was found to be 1 ppm with a linear response range of 1–100 ppm, making them potential candidates detection for CH₄ in breath and possibly also in skin. The low operating temperature employed

makes it plausible to integrate them into devices with low power consumption as well as apply them in close proximity to the body to allow for wearable sensing devices, potentially in humid environments such as breath on account of the use of the molecular sieve. Harvesting chemical and biochemical data with materials such as this, that can be integrated into wearables will open up new opportunities in the medical diagnostics space. The sensors developed here hold great potential specifically for integration into wearables on account of their small footprint, resistance to humidity, low operating temperature and relevance of methane as a biomarker in health diagnostics.

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