

IN-SITU GROWN MULTI-WALLED CARBON NANOTUBE ON INTERDIGITATED ELECTRODES FOR CARBON DIOXIDE SENSING

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Abstract

This study analyses the sensing response of multi-walled carbon nanotubes for carbon dioxide sensing. The multi-walled carbon nanotubes were grown in-situ on tungsten interdigitated electrodes. Batches with varying nanotube diameters and network densities were tested in a controlled gas chamber and tested alongside commercially available carbon dioxide sensor. Results show the promising utilisation of as-grown multi-walled carbon nanotubes for the detection of carbon dioxide without the use of microheaters. This translates to the possibility of creating small environmental sensors that can be readily integrated into existing electronic devices and made into ubiquitous low power sensors.

Keywords: Carbon dioxide sensor, Carbon nanotubes, Multi-walled.

1. Introduction

Nanomaterials have received great interest for sensing applications attributed to their nanostructured size that allow nanomaterials to have a heightened sensing capability with fast response. With current technological advances in scientific characterisation tools, nanomaterials can be explored much more closely thus allowing the behaviors and functionality of nanomaterials to be correlated better with changes of the nanomaterials' characteristics; whether physical, electrical or chemical. Nanomaterials based sensors have demonstrated very sensitive analyte detection levels as low as part per billion (ppb) [1-7]. One such nanomaterial that shows good promise are carbon nanotubes [1-2]. At current research efforts have focussed mostly on single-walled carbon nanotubes (SWCNTs) for chemical, gas and biological sensing. In this study, we focus on the aspect of gas sensing using multi-walled carbon nanotubes (MWCNTs) based on the physisorption or chemisorption of the analyte gases [4-8].

In general, adsorption of the analyte typically causes a change in the electrical conductivity of the material based on 3 different possibilities. Adsorption on the wall through defect sites or functionalised regions of the carbon nanotube wall results in localised changes of the electrical characteristics, such as the formation of dipoles and the shifting of the band structure which in turn causes a change in the conductivity of the carbon nanotube. Another possible effect of exposure to the analyte gas are the modification of the Schottky barrier interface between the carbon nanotube and the electrode contact material.

In the study here spaghetti like MWCNTs is grown in-situ on interdigitated electrodes (IDE) and then subjected to a gas testing chamber to determine its response with the presence of CO₂ diluted in N₂. Commercial CO₂ gas sensors typically employ IR (Infrared) technology, however, such sensors require the need for additional optical systems or spectrographic apparatus for analysing the change in the IR absorption. These apparatus tend to be bulky and expensive.

The MWCNTs on IDEs studied in this paper is targeted at applications in environmental monitoring such as used in greenhouses and livestock which requires ranges from 300-5000ppm CO₂ to be monitored. However such a sensor need not be limited to agriculture purposes and has possible applications in areas such as long shelve-life packaging, indoor monitoring or even health monitoring.

2. Experimental Method

The device fabricated in this study is based on electrical transduction in which the gas analyte adsorbs onto the sensing material thus resulting in proportional changes to the material characteristics. The fabrication of the MWCNT IDE device is achieved using MIMOS 8" CMOS fabrication processes while the nanomaterial is synthesized with the Oxford Instruments Nanofab 700. In the work here, the nanomaterial synthesis processes are deliberately kept as the final process to reduce the contamination (due to the nanomaterials) to the well-established CMOS processes.

To synthesize MWCNTs, a buffer layer such as aluminum oxide Al₂O₃, titanium nitride TiN or indium tin oxide ITO is typically used to prevent the catalyst material from diffusing away during the high temperature (600-700°C) processes as required for synthesis. Typical catalyst material for carbon nanotubes include iron Fe, nickel Ni, and cobalt Co but for this study, only Co is used as the catalyst

material. Figure 1(a) depicts the annealed Co catalyst material before being subjected to the MWCNT synthesis process, which shows the formation of catalyst nanoparticles needed as the seed for the MWCNT synthesis. Synthesis of MWCNTs begins when the annealed catalyst seed is subjected to a ratio of Acetylene to Ammonia ($C_2H_2:NH_3$) of 20sccm:60sccm at 700°C at a chamber pressure of 500mTorr. Acetylene act as the carbon feedstock for the MWCNT synthesis while ammonia is used in conjunction to reduce the formation of undesirable carbon formation such as amorphous carbon, a-C [3]. In this study, Co catalyst thicknesses used were 2nm, 4nm, and 6nm which produced the respective range of MWCNT diameters, as measured by scanning electron microscope (SEM), of 10-20nm, 30-50nm and 50-80nm. The thicker catalyst layer leads to larger seed sizes thus resulting in greater MWCNT diameters. For the synthesis of MWCNTs the deposition time was varied between 5s to 5mins to attain varying densities of MWCNTs growth or forests.

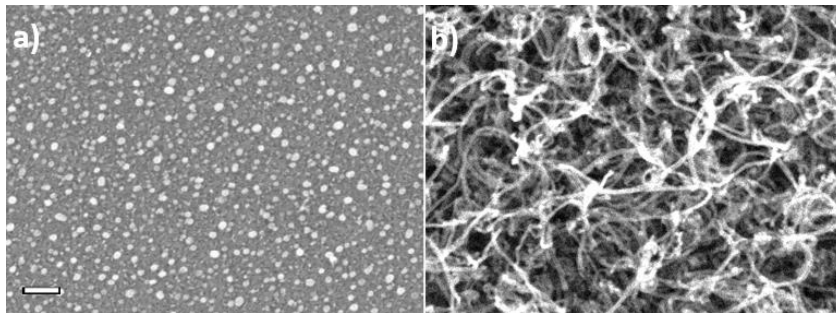


Fig. 1. (a) Catalyst seed formation from an initial thickness of 2 nm Co after annealing at 700 °C Scale bar: 100 nm, (b) Formation of MWCNTs from the Co catalyst seed

In order to fabricate the IDE device, the processes used were etched back processes. The etch back processes are industry standard for CMOS processing as it leaves a cleaner device structure formation as compared to a lift-off process typically used in research. The device fabrication starts with a blanket deposition of tungsten W (100nm) followed by titanium nitride TiN (5nm) on a silicon wafer (Si) with a top oxide layer of 300nm SiO_2 . The electrodes and bond pads are patterned by masking and exposure to UV lithography. Upon developing, exposed regions surrounding the patterned electrodes are subjected to etchant gasses which removes the TiN and W. The anisotropic etching of the exposed TiN/W occurs all the way down to the SiO_2 layer hence forming interdigitated electrodes which are electrically isolated.

The next stage is to then grow MWCNTs bridges between the electrically isolated IDEs. For synthesizing the MWCNTs a thin layer (4nm) of the catalyst material, cobalt (Co) is blanket deposited across the wafer and then etched back to remove the Co catalyst from all regions except for the active region of the IDE. As part of the verification process, the IDE structures were electrically measured after annealing of the catalyst layer to demonstrate that the IDEs were still electronically isolated. Measurements reveal resistances of the order of hundreds of k Ω . The IDEs after MWCNT growth is shown by the magnified regions in Fig. 2. Figures 2(a) and (c) correspond to MWCNTs deposited according to a deposition time of the

30s while Figs. 2(b) and (d) corresponds to a deposition time of 5 minutes. The images clearly demonstrate denser growth for longer deposition times.

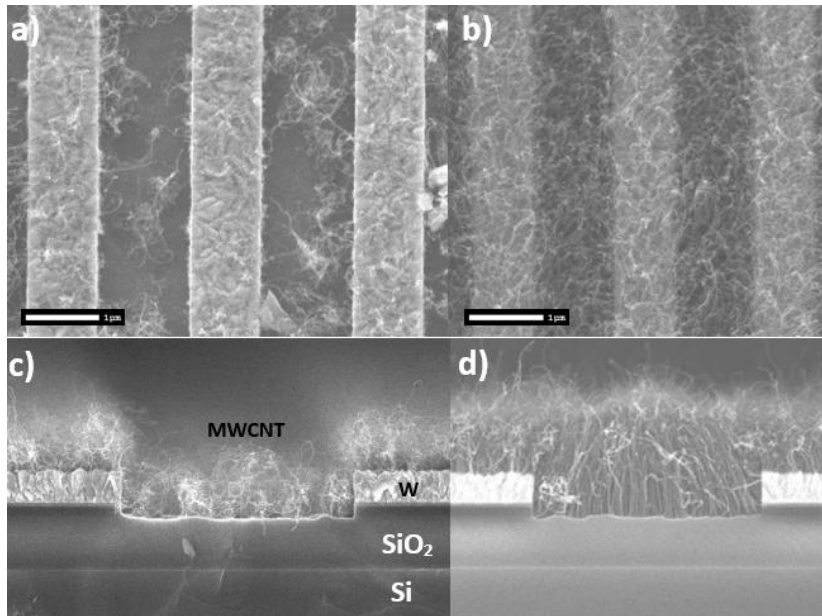


Fig. 2. Top view of MWCNT formation on IDE with deposition time: (a) 30 s and (b) 5 mins. Scale bar: 1 μ m. Corresponding cross-section view, (c) 30s, and (d) 5 min.

The feature of the IDEs is based on an electrode width of 1 μ m, spaced at 1 μ m apart and spanning an area of 3 x 3 mm as shown in Fig. 3. As the devices were fabricated on a large substrate each active device is diced and packaged as shown by the inset in Fig. 3.



Fig. 3. IDE device with 1 μ m width electrodes. Scale bar: 1 mm (Inset: Wire bonded device)

Upon completion of packaging and wire bonding of each die, the packaged devices were then tested with an in-house gas testing chamber shown in Fig. 4. For benchmarking purposes, the IDE sensor device is also tested concurrently with other commercial sensors (Figaro-polymer based sensor and Vernier-IR based sensor).

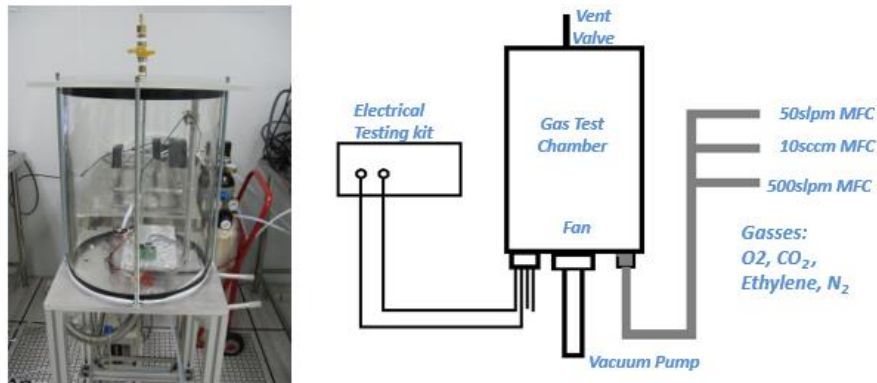


Fig. 4. Gas test chamber setup.

During the testing stage, the system is first evacuated for 1 hour and then flushed with nitrogen. The chamber valve is toggled and a chamber pressure of 500mbar is maintained. Throughout the process, a fan is continuously utilised to circulate the molecules in the chamber. This pre-conditioning is done to remove ambient air and to create the testing conditions without the presence of other analyte gasses. The chamber is left to stabilise for 10 mins and then CO₂ flows precisely into the testing chamber with a mass flow controller (MFC). As CO₂ flows into the chamber, the fan is kept running to circulate the gasses in the chamber. Upon reaching the preset CO₂ ppm level the fan is then turned off. Testing is performed for CO₂ ppm ranging from 250ppm to 2000ppm. The preset ppm testing levels were established prior to actual testing through calculations of gasses introduced to the chamber and based on readouts of the commercial sensors.

3. Results and Discussion

The MWCNT IDE gas sensor was tested with two main variations of MWCNTs; the first being MWCNT diameters and the second MWCNT densities between electrodes. Diameter variations were achieved utilising different starting thickness of Co catalyst. With a thickness of 2nm Co, MWCNTs ranging from 10-20nm were produced while 4nm Co-produced 30-50 nm diameter MWCNTs and MWCNTs diameters of 50-80nm from 6nm Co. For the variation of MWCNT density between the electrode, this is achieved by varying the MWCNT deposition times during the synthesis process as shown previously in Fig. 2(a) 30 s deposition time and Fig. 2(b) 5 min deposition time. Clearly shown is the sparsely dense MWCNT bridge network formation due to the shorter deposition time.

For the dense MWCNTs, gas testing measurements revealed the material to be highly conductive and did not demonstrate any significant responses when tested with CO₂. This is also true for sparsely grown MWCNT IDE devices but with larger diameter MWCNTs as shown by the graph in Fig. 5(a). However, the sparsely

dense MWCNT IDE with MWCNT diameters of 10-20nm showed significant changes when exposed to varying CO₂ ambient conditions.

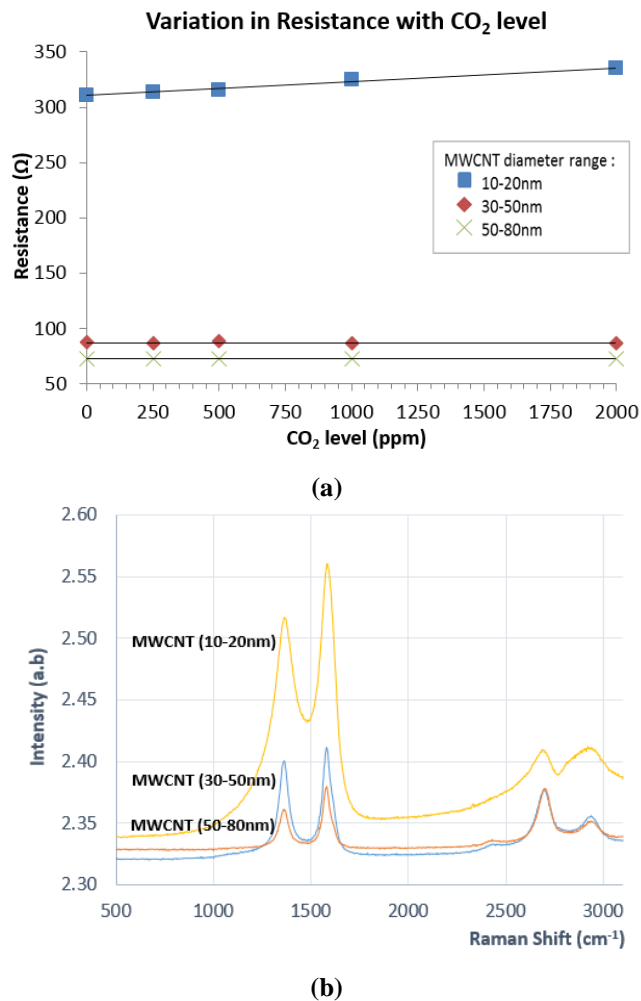


Fig. 5. (a) Resistance change for sparsely deposited MWCNTs with varying diameters. (b) Raman spectra for MWCNT batches for corresponding diameter range.

For the MWCNT IDE sensor, measurements were based on resistance changes of the sensing material. This is captured by directly measuring the potential variations across the IDE with the aid of a potential divider. The potential variations are measured using an Agilent data logger that captures the potential changes throughout the gas testing stage. The resistance as measured for the IDE for initial MWCNT sensing material with no CO₂ present starts at an average of 300Ω and shows a linear response to about 350Ω as the CO₂ levels were increased to 2000 ppm.

Figure 6 shows is the sensing response of the MWCNT IDE scaled in proportion to the expected ppm level based on the resistance of the MWCNT IDE. The response

shows that the MWCNT sensing material is able to reflect close to the expected CO₂ ppm ambient and is able to maintain its reading or resistance value without drift when the chamber conditions are maintained at the preset CO₂ ppm levels.

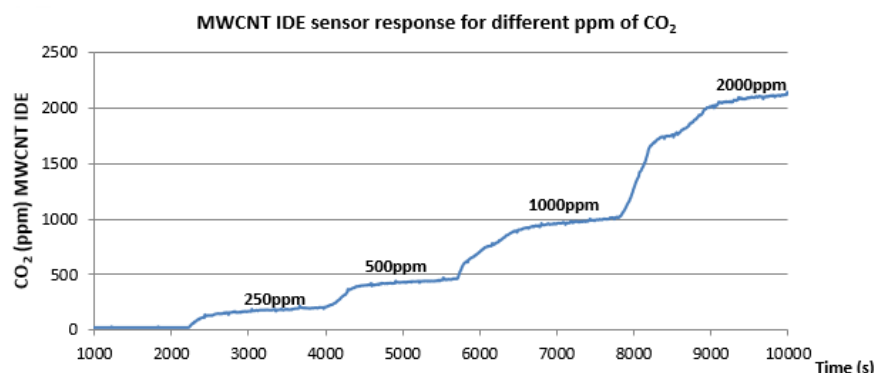


Fig. 6. The vertical axis is based on the calibrated ppm value corresponding to the resistance of the MWCNT IDE sensor device. The labels of 250 ppm, 500 ppm, 1000 ppm and 2000 pm are the expected actual values based on the commercial sensor.

This study indicates that the as-grown MWCNT responds to changes in CO₂ levels with increasing values of resistance at higher CO₂ levels.

In the testing stages, the MWCNT IDE sensing material is not heated hence chemisorption could not occur due to the high binding energy that would be required. Physisorption of CO₂ on the MWCNT wall is the likely situation for the sensing mechanism. As the CO₂ molecule is a non-polar molecule, electronegativity is not the strongest explanation for the change of resistivity. One interesting observation to note is that the G/D peak is actually lower for the 10-20nm diameter MWCNT (G/D ratio 1.15) as compared to 50-80nm MWCNTs (G/D ratio 1.47) which indicates a greater amount of defects for MWCNTs of 10-20nm. Hence a possible conclusion is that the attachment of CO₂ at such defect sites creates localised charge distribution which could result in a charge transfer between the CO₂ molecule to the nanotube due to localised effects [9-10]. Another possible explanation is molecular strobing which shifts the conduction band of the CNT. Such effects have been postulated in other studies based on the exposure of CNTs to NO₂ gas [9].

4. Conclusions

The results in this study demonstrate that in-situ deposited networks of MWCNTs on tungsten IDE are able to perform as a CO₂ sensor for ranges of ppm of 200-2000ppm which is ideal for agricultural or environmental monitoring. The adsorption of CO₂ onto MWCNTs networks revealed an increase in resistance which could be attributed to the adsorption of CO₂ at defect sites along the MWCNT wall. In order to elucidate such understanding of the sensing mechanism an in-situ technique possibly spectrograph techniques would be required to characterise the sensing material and also gas analyte characteristics immediately when the gas analyte is adsorbed onto the wall of the MWCNTs. Possibly Raman

or UV-Vis spectrograph could be acquired at rapid intervals during the gas testing stage to observe changes to the bond structure of either the localised MWCNT sites or of the adsorbed gas analyte.

Possibly, by using plasma processing greater defect sites could be created to increase the sensing response of the MWCNT network towards CO₂. Future work will involve the analysis of plasma processed MWCNT networks and also the attachment of functional groups [11] to understand the increase the response of the sensor and affinity towards CO₂.

References

1. Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.J.; Petit, P.; Robert, J.; Xu, C.H.; Lee, Y.H.; Kim, S.G.; Rinzler, A.G.; Colbert, D.T.; Scuseria, G.E.; Tomanek, D.; Fischer, J.E.; and Smalley, R.E. (1996). Crystalline ropes of metallic carbon nanotubes. *Science*, 273(5274), 483-487.
2. Avouris, P.; Appenzeller, J.; Martel, R.; and Wind, S.J. (2003). Carbon nanotube electronics. *Proceedings of the IEEE*, 91(11), 1772-1784.
3. Huang, Z.P.; Xu, J.W.; Ren, Z.F.; and Wang, J.H. (1998). Growth of highly oriented carbon nanotubes by plasma-enhanced hot filament chemical vapor deposition. *Applied Physics Letters*, 73(26), 3845-3847.
4. Kong, J.; Franklin, N.R.; Zhou, C.; Chapline, M.G.; Peng, S.; Cho, K.; and Dai, H. (2000). Nanotube molecular wires as chemical sensors. *Science*, 5453, 622-625.
5. Modi, A.; Koratkar, N.; Lass, E.; Wei, B.; and Ajayan, P.M. (2003). Miniaturized gas ionization sensors using carbon nanotubes. *Nature*, 424, 171-174.
6. Zaporotskova, I.V.; Boroznina, N.P.; Parkhomenko, Y.N.; and Kozhitov, L.V. (2016). Carbon nanotubes: Sensor properties. A review. *Modern Electronic Materials*, 2(4), 95-105.
7. Lin, Z.-D.; Young, S.-J.; and Chang, S.-J. (2015). CO₂ Gas sensors based on carbon nanotube thin films using a simple transfer method on flexible substrate. *IEEE Sensors Journal*, 15(12), 7017-7020.
8. Wang, Y.; and Yeow, T.W. (2009). A review of carbon nanotubes-based gas sensors. *Journal of Sensors*, Article ID 493904, 24 pages.
9. Li, J.; Lu, Y.; Ye, Q.; Cinke, M.; Han, J.; and Meyyappan, M. (2003). Carbon nanotube sensors for gas and organic vapor detection. *Nano Letters*, 3(7), 929-933.
10. Watts, P.C.P.; Mureau, N.; Tang, Z.; Miyajima, Y.; Carey, J.D.; and Silva, S.R.P. (2007). The importance of oxygen-containing defects on carbon nanotubes for the detection of polar and non-polar vapours through hydrogen bond formation. *Nanotechnology*, 18(17), 6 pages.
11. Yu, H.; Cao, T.; Zhou, L.; Gu, E.; Yu, D.; and Jiang, D. (2006). Layer-by-layer assembly and humidity sensitive behavior of poly (ethyleneimine)/multiwall carbon nanotube composite films. *Sensors and Actuators B: Chemical*, 119(2), 512-515.