

# Fabrication of MWCNTs Based Oxygen Gas Sensor using CCVD technique

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**ABSTRACT:** The work aims at fabricating multi walled carbon nanotubes (MWCNTs) based sensor for sensing Oxygen gas. The high quality MWCNTs were chemically synthesized by using Catalyst Chemical Vapour Deposition (CCVD) method with simultaneous treatment of Fe/Mo/Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of Hydrogen and Acetylene at 850°C. MWCNTs was coated on the glass substrate using a polymeric mixture and electrical contacts were made using a silver paste in order to measure the resistance. The surface morphology of sensor studied using Scanning Electron Microscope (SEM) and depicts the diameter of MWCNTs to be ~ 50 to 200 nm. For the various concentrations of Oxygen gas the resistance of the MWCNTs was found to decrease with time. This phenomenon was understood on the basis of Oxygen–Carbon interactions. The sensitivity of the device improves significantly with increase in gas concentration inside the chamber. Maximum sensitivity of about 2.0903% was achieved for the presently synthesized MWCNTs, with response and recovery times of about 10 s and also shows the repeatability and reproducibility.

**KEYWORDS:** Catalyst Chemical Vapour Deposition, MWCNTs, Oxygen Gas Sensor, SEM.

## I. INTRODUCTION

Recently a lot of research has been done on Gas sensors for various industrial demands like sensitivity, selectivity, faster response and recovery time etc. which could be employed in the manufacturing and processing units for monitoring as a safety regulator. Nanotechnology has helped us to design sensors which are cost efficient, flexible and low on power consumption. Gas sensors have found its applications in mostly all fields be it electronics or biotechnology, in space shuttles or toxicity control in nature, pharmacy or food industry. [1] The two main parameters are high sensitivity and selectivity which is required for tracking the real-time detections of toxic or volatile gases in industries. The sensitivity of the device has increased due to increase in adsorption of gas molecules which has been contributed by the hollow nanostructured materials, in turn affects the surface to volume ratio.

In 1991, Iijima discovered Carbon nanotubes. [2] The gas sensing property of MWCNTs, are theoretically understood due to gas adsorption and the effects of collision on the surface of nanotubes. [3], [4] Here we would like to understand how Multi walled Carbon nanotubes (MWCNTs) interact with oxygen gas molecules based on its geometry and morphology. [5] When compared to graphite, MWCNTs have asymmetric distribution of electrons on the surface because of their morphology. [6] This results in increase of their electrochemical behavior due to rich  $\pi$ -electron conjugation. [7], [8] The device is fabricated in order to detect the presence of gases in a specific area. [9] It can be employed as safety instrument, to avoid leakage and monitor toxicity. The gas taken for study was oxygen gas, though the study is not toxicity related.

Gas sensor measures and indicates the concentration of certain gas. It interacts with certain gases and each gas has its unique breakdown voltage [10], i.e the electric field at which it is ionized. Sensor identifies gases by measuring these

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voltages. The concentration of gas can be determined by measuring the resistance from device due to current flow. The electrical properties i.e resistance can be alternated by adjusting the size of nanostructured materials and the cross sectional area which is exposed for gas interaction.[10] The electrical resistance of the sensor is attributed to the potential barrier in the presence of deoxidising gas, the surface density of negatively charged oxygen decreases so that the barrier is reduce. This in turn decreases the sensor resistance, thus the concentration of deoxidising gas can be expressed by following the equation, and sensitivity can be calculated.

The work highlights that such a sensor could prevent the oxide formation, if installed in a synthesis unit. The sensitivity and resistance contributed by this device are studied by using gas sensor. The nano structured material that is MWCNTs are employed, due to their high surface to volume ratio. Here we shall discuss the synthesis of high quality Multi walled carbon nanotubes (MWCNTs) for their oxygen gas sensing properties. The MWCNTs were successfully synthesized by using Catalyst Chemical Vapour Deposition (CCVD) method and were characterized by Scanning Electron Microscope (SEM) for their micro structural behaviour.

## II. MATERIALS AND METHODS

The MWCNTs were synthesized by Catalyst Chemical Vapour deposition (CCVD) method by using Hydrogen and Acetylene gases simultaneous at 850°C for about 3-4 hours. The catalyst employed was Fe/Mo/Al<sub>2</sub>O<sub>3</sub> in desired ratios. The MWCNTs achieved by this process were purified using few acids, in order to remove the un-reacted catalyst. The MWCNTs were air dried in hot air oven at an optimum temperature of about 30°C. [11]

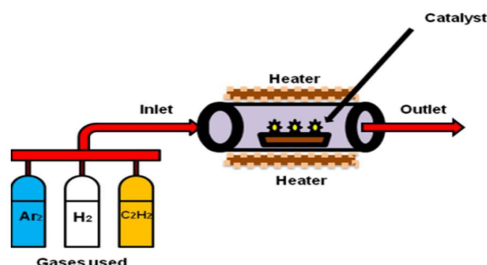


Fig.1 Schematic representation of the growth of MWCNT's using CCVD technique, by employing Fe/Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The process involved simultaneous supply of Argon, Hydrogen and Acetylene gases at 850°C. respectively.

The device was fabricated by taking a pinch of pure MWCNTs, and dispersing them in a polymeric mixture. The polymeric mixture was added in order to provide the necessary adhesion between the glass substrate and the nanostructured materials. The supernatant was prepared by taking 2g of polystyrene (thermocool) in 20ml of Toulene. The MWCNTs were ultrasonicated in this mixture for 3 min. The solution was coated on the glass substrate by doctor blading technique.

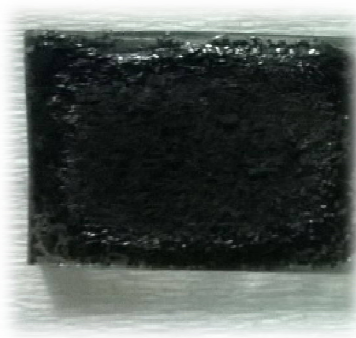


Fig.2 Photograph of the sample, consisting of MWCNTs which were synthesized using CCVD technique. It was coated on glass substrate using a polymeric mixture before carrying out the experiment.

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## III. EXPERIMENTAL SETUP

The device fabricated is kept in the gas sensor chamber unit, the furnace is switched ON, and its heated up to 200°C. Initially the Argon gas (10ppm) is sent into the chamber for about 30 min. The reactant gas is sent into the chamber, for different concentrations. In this work, Oxygen gas is the reactant gas, and the different concentrations of study are 10ppm, 20ppm, 30ppm for 10 seconds respectively. The oxygen gas supply is cut off, and Argon gas is sent in order to stabilize the gas chamber. The resistance was measured using Impedance Analyser.

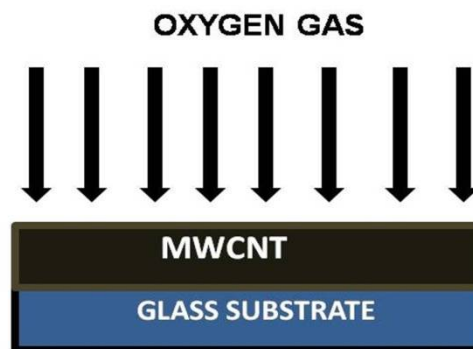


Fig.3 The schematic representation of MCNTs coated on a glass substrate using a polymeric mixture is exposed to different concentrations of oxygen gas in a closed chamber. The device operates at an optimum temperature of 200°C.

Different parameters were studied in order to understand the working of this device. Data was analysed and graphs were plotted between Resistance and Time, Sensitivity and Concentration of oxygen gas.

The sensitivity is calculated

$$S = \frac{R_g - R_o}{R_o} \times 100$$

S = Sensitivity (%)

$R_g$  = Resistance of gas sensor after exposed to Oxygen gas. (ohm).

$R_o$  = Resistance of gas sensor without exposure of Oxygen gas. (ohm)

$R_{g1}$ ,  $R_{g2}$ ,  $R_{g3}$  at different concentrations of Oxygen gas- 10ppm, 20ppm , 30ppm respectively.

The device runs at constant voltage of 5V, for constant time = 10 second.



Fig.4 The MWCNTs coated glass substrate was placed inside the Gas sensing unit. The fabricated device is exposed to different concentrations of Oxygen gas. The change in the resistance was observed and the sensitivity of the device was calculated.

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## IV. EXPERIMENTAL RESULTS

MWCNTs based gas sensor display high uniformity and sensitivity to oxygen gas. These sensors have faster response and recovery time, but after increasing the gas concentrations with lesser difference they tend to saturate or show minimal difference. But the resistance increases with respect to time factor. When electrons withdrawing molecules of Oxygen interact with P-type MWCNTs, they tend to change the density of the main charge carriers, i.e holes in the bulk of the nanotube which changes the conductance of the MWCNTs. [12]

### 4.1 SURFACE CHARACTERIZATION

MWCNTs were characterized by Scanning Electron Microscope (SEM) for their micro structural behaviour. MWNTs have been reported to have diameters of roughly 10 to 200 nm and are few microns long. They have been stated to have high aspect ratios and high electrical conductivity.[12]

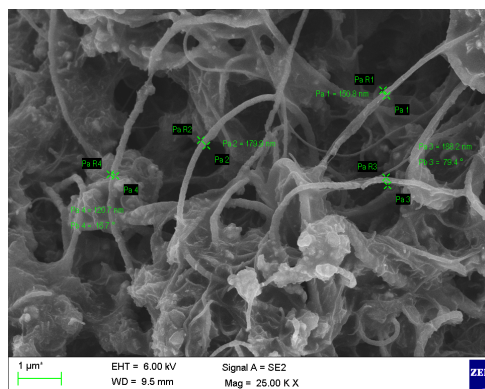


Fig.5 The MWCNTs synthesized using CCVD technique were characterized using Scanning Electron Microscope. The SEM image of MWCNTs of magnification range 25.00 KX is analysed. The MWCNTs were observed to be non uniform in nature. The diameter of nanotubes were found to be ~50 -200 nm

When an oxygen molecule interacts with MWCNTs it will get adsorbed onto the surface of MWCNTs. The O<sub>2</sub> molecules have high diffusion kinetics on nanotube surface. Electron density analysis shows that charge transfer is induced from Carbon atom to the O<sub>2</sub> gas molecule leading to hole doping of semiconducting nanotube. The increase in hole carriers in the MWCNTs are responsible for the increase in conductance. [13]

### 4.2 ELECTRICAL CHARACTERIZATION:

Research has been done to understand the electronic properties of MWCNTs which are very sensitive to their chemical response with oxygen gas. [14] The electronic properties of MWCNTs when exposed to oxygen gas theoretically using the ab initio pseudo potential total energy method.

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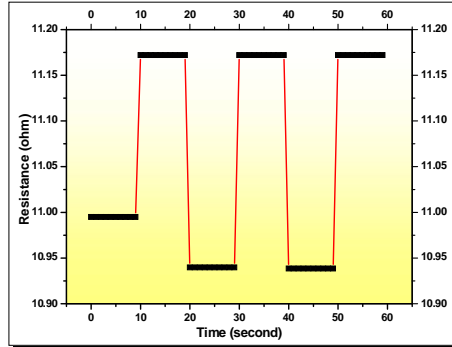


Fig.6 Dynamic gas response of MWCNTs thin film at 60°C was studied. The sensitivity of the device was calculated based on the resistance which was achieved when exposed to various concentrations of gas. The sensitivity was increased from 1.5852% to, 2.0793, and 2.0903 respectively.

These results proved that MWCNTs act as sensitive gas sensors [15] The oxygen carbon interactions are due to the charge transfer between the oxygen gas molecules which act as electron donors and the MWCNTs act as electron acceptors.[16]

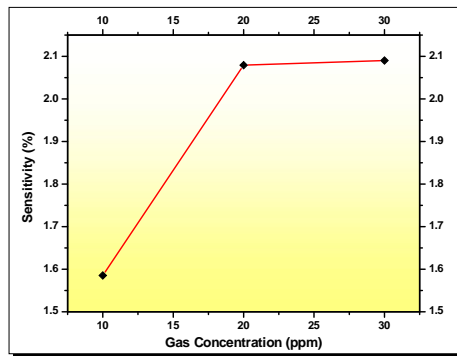


Fig.7 Sensitivity response of MWCNT reaches 1.5852% at 10 ppm of oxygen gas exposure. As we increase the oxygen gas concentration to 20ppm the sensitivity of the device shoots up drastically to 2.0793%. The sensitivity of the device saturates when 30 ppm of oxygen gas is passed into the chamber. The maximum sensitivity achieved was at 2.0903%.

The adsorption of oxygen gas molecules on MWCNTs are understood by density functional theory (DFT) .The gas adsorption is decided by the site availability and binding energy of the oxygen gas molecule.

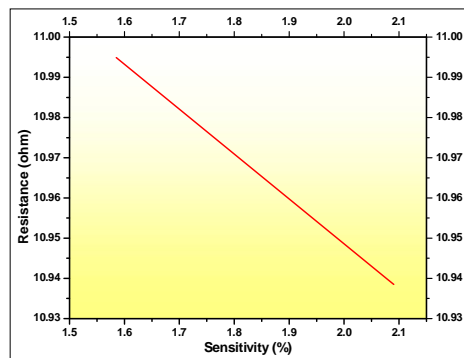


Fig.8 The resistance of the device initially was measured and found to be 11.17202Ω. When the device was exposed to various concentrations of oxygen gas the resistance of the device decreased whereas the sensitivity improved gradually. The electrical response of MWCNTs based gas sensor was studied. The device was tested for its stability and repeatability and the device was optimized to function at 200°C.

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Basically the gas adsorption depends on the external surface and the interior pore present on the MWCNTs. [17] The recovery time was about 2 hours but can be intensively reduced by heating the substrate at 200°C. The device was checked for its repeatability and stability.

## V. CONCLUSION

Our results show MWCNTs has the potential to be an excellent gas at room temperature provided it should be exposed to gas concentration of higher difference. The resistance of the MWCNTs was found to decrease with time for all the concentrations under study. This has been understood on the basis of Oxygen – Carbon interactions. Gas sensitivity was estimated and the sensitivity gets improved with increase in concentration of the gas inside the chamber. [13] Maximum sensitivity obtained for the presently studied MWCNTs is found to be approximately 2.0903%. The sensitivity of the MWCNTs gas sensor has been discussed not selectivity factor of the gas sensor. The future work will concentrate on further enhancing the performance of MWCNTs with respect to the different gases exposed. The selectivity property of the pristine MWCNTs sensor is limited to the molecules that have large binding energies and charge transfers with the nanotubes hence doped MWCNTs are used for sensing a range of molecules.

We have employed pristine MWCNTs of ~ 50 to 200nm diameter and few microns long for our oxygen gas sensor, but the sensitivity of this device could be improved by using functionalized MWCNTs. The response and recovery times of about 10 s and also shows the repeatability and reproducibility. Doping of MWCNTs with metal nanoparticles can also drastically improve the sensitivity response of this device. Instead of coating MWCNTs on a glass substrate we could make it more flexible and more efficient by employing conducting polymers. [13]

## REFERENCES

- [1] Aliofkhazraei, M., Ali, N., "Recent Developments in Miniaturization of Sensor Technologies and Their Applications", Materials Science and Materials Engineering, vol.13, pp.245-306, 2014.
- [2] Iijima, S., "Helical microtubules of graphitic carbon", Letter to Nature, vol.354, no.6348, pp.56-58, 1991.
- [3] Sinha, N., Ma, J., Yeow, J. T. W., "Carbon nanotube-based sensors", Journal of Nanoscience and Nanotechnology, vol.6, no.3, pp.573-590, 2006.
- [4] Li, J., Ng, H. T., "Carbon nanotubes sensors", Encyclopedia of Nanoscience and Nanotechnology, vol.1, pp.591-601, 2004.
- [5] Wang, Yun, John T. W. Yeow, "A Review of Carbon Nanotubes-Based Gas Sensors", Journal of Sensors, 2009.
- [6] Girard-Lauriault, Pierre-Luc, Illgen René, Ruiz, Juan-Carlos, Wertheimer Michael, R., Unger Wolfgang, E. S., "Surface functionalization of graphite and carbon nanotubes by vacuum-ultraviolet photochemical reactions", Applied Surface Science, vol.258, no.22, pp.8448-8454, 2012.
- [7] Meyyappan, M., "Carbon Nanotubes: Science and Applications", CRC Press, Boca Raton, Fla, USA. 2004.
- [8] Michalitsch, R., Kassmi, A. El., Yassar, A., Lang, P., Garnier, F., "Increase of conjugation length within SAMs of terthiophene-derivatives, through electrochemical intermolecular coupling", Journal of Electroanalytical Chemistry, vol.457, no.1-2, pp.129-139, 1998.
- [9] Gopinath, P. G., Anitha, V. R., Mastani, Aruna S., "Microcantilever based Biosensor for Disease Detection Applications", Journal of Medical and Bioengineering, vol.4, no.4, pp.307-311, 2015.
- [10] Andrei Kolmakov, Martin Moskovits, "Chemical Sensing and Catalysis by One-Dimensional Metal-Oxide Nanostructures", Annual Review of Materials Research, vol.34, pp.151-180. 2004.
- [11] Thi Thanh Cao, Thi Thanh Tam Ngo, Van Chuc Nguyen, Xuan Tinh Than, Ba Thang Nguyen, Ngoc Minh Phan, "Single-walled carbon nanotubes synthesized by chemical vapor deposition of C<sub>2</sub>H<sub>2</sub> over an Al<sub>2</sub>O<sub>3</sub> supported mixture of Fe, Mo, Co catalysts" Advances in Natural Sciences: Nanoscience and Nanotechnology, vol.2, no.3, 2011.
- [12] Ting Zhang, Syed Mubeen, Nosang V., Myung, Marc A., Deshusses, "Recent progress in carbon nanotube-based gas sensor", IOP science, vol.19, no.33, 2008.
- [13] Jung, D., Lee, K. H., Kim, D., Overzet, L. J., Lee, G. S., "A gas sensor using a multi-walled carbon nanotube sheet to detect oxygen molecules", Journal of Nanoscience and Nanotechnology, vol.13, no.12, pp.8275-8279, 2013.
- [14] Collins, P. G., Bradley, K., Ishigami, M., Zettl, A., "Extreme oxygen sensitivity of electronic properties of carbon nanotubes", IOP Science, vol.287, no.5459 pp.1801-1804, 2000.
- [15] Jhi, S. H., Louie, S. G., Cohen, M. L., "Electronic properties of oxidized carbon nanotubes" Physical Review Letters, vol.85, no.8, pp.1710-1713, 2000.
- [16] Sumanasekera, G. U., Adu, C. K., Fang, S., Eklund, P. C., "Effects of gas adsorption and collisions on electrical transport in single-walled carbon nanotubes", Physical Review Letters, vol. 85, no.5, pp.1096-1099, 2000.
- [17] Williams, K. A., Eklund, P. C., "Monte Carlo simulations of H<sub>2</sub> physisorption in finite-diameter carbon nanotube ropes", Chemical Physics Letters, vol.320, no.3-4, pp.352-358, 2000.