Nanomaterials in Sensors

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***Abstract*-In this work a reliable, satiable gas sensor incorporating single walled carbon nanotube (SWCNT) as sensor element for the detection of toxic gases is presented. We described the different fabrication technique like arc discharge method, laser ablation and chemical vapor deposition technique of a SWCNT sensor for the detection of various toxic gases. We mainly focused on the CVD technique as it is the most efficient and promising technique for the synthesis of SWCNTs. An experimental work cited by different research groups is also explained in this work.**

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Keywords: ablation, CVD, laser, nanotube,sensors, SWCNT, toxic.

I. INTRODUCTION

The atmospheric air we live in contains various poisonous substances that adversely affect our environment and health. So there is a need to detoxify such gases.For detoxification we need to first detect the gas and we all are aware that the detection of biological and chemical species in atmosphere or process gases is of a great concern in relation to environmental pollution.Thus the development of a reliable, satiable and inexpensive sensor that can take the advantage of nanoscale for sensing toxic gas in real time with good sensing performance is the focus of many research groups. It has gained an increasing attention for the safety purpose and for a pollution free environment. Emerging nanotechnologies offer an unprecedented promise for sensors: smaller and weight, lower power requirement, more sensitivity and more specificity. Manychemical based nanosensors like ZnO,TiO_2,CuO, single walled carbon nanotube (SWCNT) have been developed yet for sensing various toxic gases such as carbon monoxide,nitrous oxide,hydrogen,ammonia etc. Out of this carbon monoxide,ammonia and nitrous oxide are the key components of the polluted air. So this paper basically focuses on the detection of these particular gases for environmental monitoring.

Gas sensors with high sensitivity and selectivity are required for leakage detections of toxic gases and for real-time detections oftoxic or pathogenic gases in industries.in this study gas sensor employing swcnt as sensor element was introduced for CO and NH3 because of their large surface area with the excellent sensitivity and fast responses at room temperature.Single-wall carbon nanotubes (SWCNTs) are considered as one of the majorcandidate materials because of their excellent characteristics.SWNTs are an allotrope of sp2 hybridized carbon similar to fullerenes. The structure can be considered as a cylindrical tube comprised of 6-membered carbon rings, as in graphite. The cylindrical tubes may have one or both ends capped with a hemisphere of the buckyball or fullerene structure .Carbon nanotube sensors can also be used for sensing ethanol,methanol and even volatile organic compounds.the only problem with swcnt is that CNT-based chemical sensors normally have a long recovery time (upto several hours) to release the analytes for another sensing operation. Poor recovery remains a drawback for CNT-based chemical sensors recovery but if it is exposed to an ambient temperature then the mentioned problem may be overcome.

In this work we have described the synthesis of swcnt by chemical vapour deposition mthod. There are many methods for the synthesis of swcnt like arc discharge method, removal of catalyt,laser ablation,chemical vapour depostion but of the various means for SWCNTs synthesis, CVD is the most promising or effective technique to the manufacture of larger SWNTs quantities because it has a relatively low cost, a large-scalecapability, a high versatility.CVD is capable of growing nanotubes directly on a desired substrate, whereas in the other growth techniquesthe nanotubes must be collected.

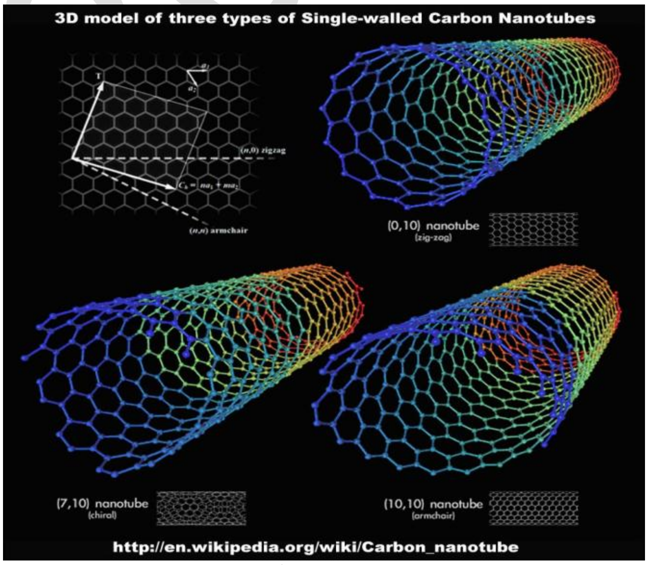

Fig.1shows the image of a single walled carbon nanotube.

II. SYNTHESIS OF SWCNT SENSOR

There are three main techniques for the synthesis of single walled carbon nanotubes i.e. arc discharge method,laser ablation and chemical vapor deposition technique. Out of which CVD is the most effective technique.

A. Arc discharge method

The carbon arc-discharge method is the first method used for growing CNTs. The process is carried out in an evacuated chamber.Two carbon electrodes act as carbon source and for increasing thespeed of carbon deposition inert gas(like helium) is being supplied. When high DC voltage is applied between the carbon anode and cathode, plasma of the inert gas is generated to evaporate the carbon atoms. The ejected carbon atoms are thendeposited on the negative electrode to form CNTs. Both SWNTs and MWNTs can be grown by this method, while the growth of SWNTs requires catalysts. It is the principal method to produce high quality CNTs with nearly perfect structures.

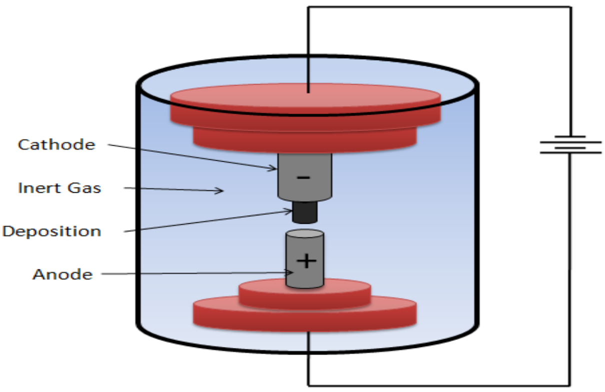

Fig.2 shows the image of arc discharge technique.

B.Laser ablation technique

In the laser ablation technique, a high power laser was used to vaporize carbon from a graphite target at high temperature. Both MWNTs and SWNTs can be produced with this technique. In order to generate SWNTs, metal particles as catalysts must be added to the graphite targets similar to the arc discharge technique. The quantity and quality of produced carbon nanotubes depend on several factors such as the amount and type of catalysts, laser power and wavelength, temperature, pressure, type of inert gas, and the fluid dynamicsnear thecarbon target. In such technique, argon gas carries the vapors from the high temperature chamber into a cooled collector positioned downstream. The nanotubes will self-assemble from carbon vapors and condense on the walls of the flow tube. The diameter distribution of SWNTs from this method varies about 1.0 - 1.6 nm. Carbon nanotubes produced by laser ablation were purer (up to 90 % purity) than those produced in the arc discharge process and have a very narrow distribution of diameters.

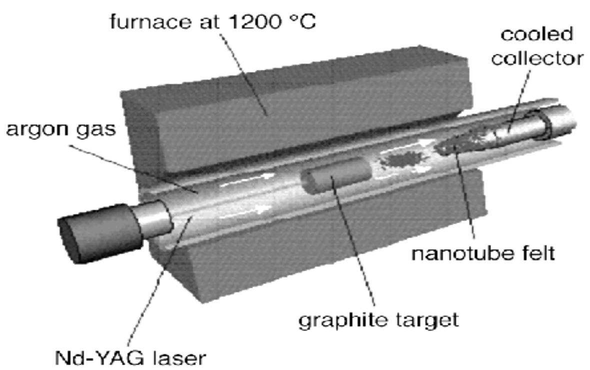

Fig.3 shows the schematic of laser ablation technique.

C. Chemical Vapor Deposition (CVD)

By chemical vapor deposition CNTs can be produced in large quantities. The process temperature can vary from 500 - 1300°C. The hydrocarbon precursors include CH_4, C_2H_2, C_6H_6, alcohols etc.

$$\textit{Hydrocarbon} + \textit{Fe} / \textit{Co} / \textit{Ni catalysts} \xrightarrow{550-1000^0 C} \textit{CNT}$$

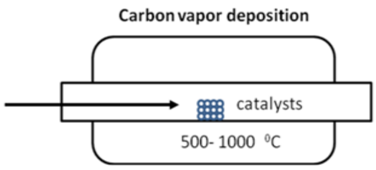

Fig.4Schematics for carbon vapor deposition method.

In CVD method there is initial dissociation of hydrocarbons followed by dissolution and saturation of C atoms in metal nanoparticles. Thereafter there is precipitation of carbon. Vapor-grown CNTs generally use metal catalyst particles. Fe, Co and Ni catalysts are mostly used for the catalytic growth of CNT. More recently, CNTs have also been grown from metal such as Au, Ag and Cu. Catalyst serves as nucleation sites and also promotes pyrolysis of hydrocarbons. Compared with thefirst two techniques; CNTs can be synthesized at relatively low temperature using CVD method.

Therefore, this technique is more efficient and allows scaling up the growth of SWCNTs. By modification and calculated control of the growth parameters, vertically aligned MWCNTs growth can be achieved by CVD technique. This enhances CNTs electronic properties in different applications. High-quality SWCNTs can also be obtained by theoptimization of the catalysts.

III. EXPERIMENTAL WORK

An experimental work performed by a research group is explained below.

A. Growth of CNTs

A silicon substrate is coated with a Ni metal which acts as a catalyst for CNT growth using thermal evaporation method. The coated samples are placed onto a heating plate in the center of the PECVD reactor, which is then pumped down to a low base pressure (~1mTorr) to evacuate atmospheric gasses. Then the substrate is heated to a temperature shown to produce carbon nanotubes (450 to 700°C depending on process and chemistry).

B. Gas Sensing Procedure

Gas sensing experiments were carried out by placing CNTs synthesized on a quartz substrate in a sealed Plexiglas test chamber with an electrical feed-trough. At first, the chamber was purged continuously with pure argon gas about 1 hour. Then, diluted CO_2 or NH_3 in the argon as a carrier gas was injected into the chamber at room temperature of 25°C. Sensor resistance was measured at intervals of 10 seconds with a digital multimeter connected to a computer using an RS232 interface that was fully automated and logged by a program. Each test is repeated for two times to obtain the exact results.

IV. RESULTS AND DISCUSSIONS

A. Structure Characterization

The samples were characterized by using Scanning Electron Microscopy (SEM). SEM micrographs have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. Fig.5. shows the SEM image of pristine sample which is taken after deposition of 100A˚ thin layer of Ni metal on Si substrate by evaporation technique.

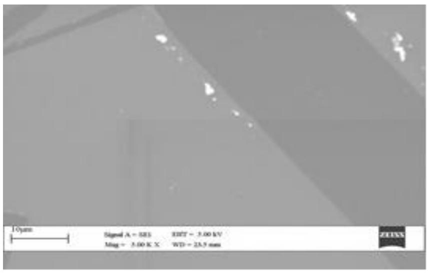

Fig.5 SEM image of pristine sample

And Fig.6 Shows the SEM image of CNTs after CVD-Process (PECVD without plasma) using a mixture of NH_3 (15sccm) and C_2H_2 (15sccm) at Reaction temperature of 7300C. From this it is clear that the growth of CNTs produced is tip-growth, where the nanotube lifts the catalyst from the substrate during the growth, as the nanotube nucleates and grows below the catalyst.

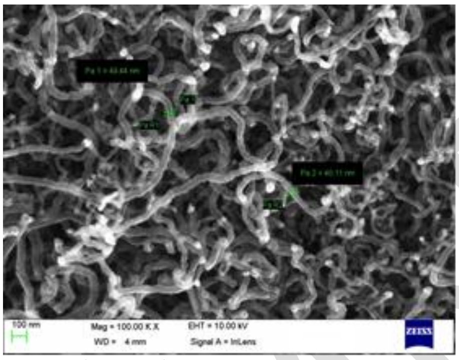

Fig.6SEM image of CNTs after CVD-Process (PECVD without plasma)

B. Gas sensing characteristics

Ammonia Absorption: The results obtained indicate that the carbon nanotubes grown were sensitive to ammonia. Upon exposure to ammonia, the resistance of carbon nanotubes increased significantly at room temperature of 25°C. Fig 7 shows the results of the samples for 2 repetitions. The maximum resistance detected is 159.8 milliohmwhich is more than the resistance recorded in argon. From the graph, it can be seen that the first repetition, R1 has a lower value compared to R2. This indicates that the absorbed ammonia gas had interacted with carbon nanotube molecules and did not desorbed immediately. R2 has a higher reading due to accumulated ammonia gas in the sample.

This result indicates that CNTs have a high affinity for ammonia due to ammonia being a polar molecule with a dipole moment of 1.5 Debye. When the samples are exposed to NH_3 gas, electrons are transferred from NH_3 to CNTs. NH_3molecules donate electrons to the valence band of the CNTs, decreasing the number of holes, thereby increasing the separation between the conduction band and the valence band.

This forms a space charge region at the surface of the semiconducting CNTs, increasing the electrical resistance. The increase in resistance proves that the CNTs are a p-type semiconductor. From results even we can say that, upon exposure to NH_3 gas, the resistance ofthe CNTs based sensor increasedwith an increase in gas concentration. It is noted that NH_3 absorbed into CNTs by replacing pre-adsorbed oxygen within the carbon atoms. Oxygen, an oxidizing gas, increases the conductivity of p-type carbon nanotubes as it increases the hole concentration; hence the replacement of oxygen by ammonia should reduce the conductivity.

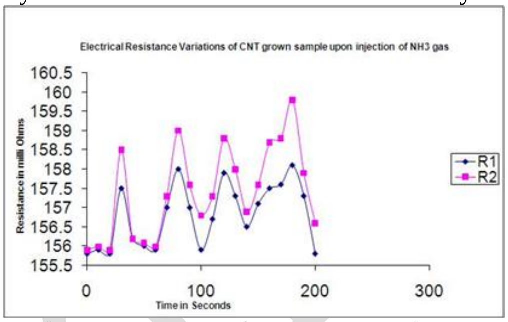

Fig 7 Electrical resistance variation of CNTs grown sample upon injection of NH_3 gas

V. CONCLUSION

Production of high yield, good quality, purified SWCNTs film using catalytic CVD technique has been described. The aim of this study was to investigate the application of carbon nanotube sensor in sensing various toxic gases. With the help of different characteristics and the experimental work we came to know about the efficiency of this sensor. It is found that SWCNT sensor is the most efficient sensor.

ACKNOWLEDGEMENT

I would like to thank my guide Prof. Shibu G. Pillai who provided me with an opportunity to present paper on this topic which lead to enhancement of knowledge.

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