CARBON NANOTUBES AND ITS APPLICATION IN MAKING GAS SENSORS

NIVEDITA PANDEY
Niveditapandey91@gmail.com
AJAY KUMAR GARG ENGINEERING COLLEGE GHAZIABAD
PAVAN KUMAR
Pawan.evergreen@gmail.com
AJAY KUMAR GARG ENGINEERING COLLEGE GHAZIABAD

Abstract-**As the technology is moving very fast the next big thing is very small-NANOTECHNOLOGY. Nanotechnology has wide application in all the sector of science and technology. In this paper we have given detail description about carbon nanotube and its properties. it also gives the how these properties can be used to design gas senors.In this paper integration of carbon nanotube (CNT)-based sensor and complementary metal–oxide–semiconductor integrated chip (CMOS IC) to detect hydrogen gas in a single chip is presented. A gas sensor comprised of a gas-responsive multiwall carbon nanotube (MWNT)—silicon dioxide composite layer deposited on a planar inductor-capacitor resonant circuit is presented here for the monitoring of carbon dioxide, oxygen, and ammonia. The absorption of different gases in the MWNT-SiO_2 layer changes the permittivity and conductivity of the material and consequently alters the resonant frequency of the sensor.**

INTRODUCTIONS

Carbon nanotubes (CNTs) are tubular structures that are typically of nanometer Diameter and many micromeres in length Because of their tiny size, these nanostructures Exhibit many interesting and often unexpected properties, and these properties have wide applications in making a nanosensor. Carbon nanotubes have found application as field emission devices, electronic switches actuators and random access memory. In addition, there is an increasing demand for the commercial utilization of this material in the industry such as highly sensitive miniaturized biochemical sensors. In this regard, the importance of integration with complementary metal–oxide–semiconductor integrated chip industry becomes greater. One can use a CMOS IC as a sensor platform and build CNT based sensors on top of it. In this paper, we also present the application of multiwall carbon nanotubes (MWNTs) for detection of carbon dioxide, oxygen, and ammonia based upon the measured changes in MWNT permittivity and conductivity with gas exposure

CARBON NANOTUBE

Carbon nanotubes (CNT) are long, thin cylinders of carbon. They were first observed by Ijima in 1991, during the direct current arching of graphite for preparation of fullerenes. Nanotube structures are made of graphite like carbon (mainly C6 ring fusions) possessing enough C5-ring fusions to allow curvature into. CNTs have remarkable electrical properties. cylindrical sheets of graphite with an aspect ratio typically greater than 100 and outer diameter measuring tens of nanometer and closed at ends with two

semi domes. Essentially, two families of carbon nanotubes exist:

(1) Single walled nanotubes (SWNT), made up of only one straight tubular unit. It is a fundamental form of carbon nanotube. The typical structures of SWNTs have been confirmed by scanning tunneling microscopy (STM) and electrical diffraction studies; cylindrical sheets of graphite with an aspect ratio typically greater than 100 and outer diameter measuring tens of nanometer and closed at ends with two semi domes.

(2) Multi walled nanotubes (MWNT) made of series of coaxial tubes 0.34 nanometer apart (same distance among the vertical planes of graphite)

PROPERTIES OF CARBON NANOTUBE

Mechanical properties-The carbon–carbon chemical bond in a graphene layer is probably the strongest Chemical bond in an extended system known in nature. Since CNTs are seamlessly rolled-up graphene layers. Graphite is exceptionally strong with respect to in-plane deformations and can support very large tension. Nanotubes have high tensile strength .Not only are nanotubes strong, but they are also extremely elastic. The atomic nature of the nanotube structure will only come into play for very large deformations or at the limit of extreme tension. One of the features of nanotubes is that their length can be macroscopic, up to millimeters, while their width falls in the nanoscale. Mechanical properties is independent of their chirality. Because of their large tensile modulus (on the order of 1 TPa), nanotubes have often been discussed as potential target components of nanoscale fiber-reinforced composites for mechanical applications such as composites.

Thermal property- As nanoscale graphitic structures, a carbon nanotube is of great interest not only for their electronic and mechanical property but also for their thermal properties. Because of their small size, quantum effects are important. At room temperature thermal conductivity over 200W/Mk for (SWNT) and over 3000W/m K for (MWNTS)

Electrical property- It has been theoretically predicted that the properties of nanotubes are sensitively dependent on the tube diameter and chiral. There are two possibilities the tubes are expected to be metallic; otherwise, they are semiconducting with an energy gap of approximately0.5 eV. In the semiconducting case, the energy gap is dependent on the tube diameter, with increasing diameters leading to decreased energy gaps. It is possible to control the band gap energy without doping.Inside CNTs, electrons are not easily scattered due reduced scattering in metallic CNTs leads to their very low resistances. Electrical properties of SWNTs can undergo extreme changes in the presence of even small concentrations of gases such as oxygen Exposure to oxygen will change the resistance by a dramatic 10%–15%, presenting a number of implication one of them is gas sensors.

Carbon dioxide oxygen ammonia gas sensors

Most gas sensors available on the market today operate by measuring the impedance of a capacitor coated with a gas-responsive polymer(s) or ceramic. These gas sensors offer a high degree of accuracy and reliable performance, but require hard-wire connections between the sensor head, power supply, and data processing electronics which precludes many monitoring applications. we have presented the application of multiwall carbon nanotubes

(MWNTs) for detection of carbon dioxide, oxygen, and ammonia based upon the measured changes in MWNT permittivity and conductivity with gas exposure. The transduction platform used in this work was a planar, inductor-capacitor resonant-circuit (LC) sensor. A thin Layer of gas-sensitive MWNT-SiO composite is placed upon the interdigital capacitor of the LC sensor; as the permittivity and/or conductivity of the adjacent MWNT-SiO composite changes, so does the sensor resonant frequency that remotely monitored through a loop antenna. The passive nature of the LC sensor enables long term monitoring without battery lifetime issues, and the wireless nature of the platform enables long-term gas monitoring from within sealed, opaque containers.

A. Preparation of Carbon Nanotubes

The MWNTs used in making gas sensor work were prepared by pyrolysis of ferrocene and xylene under Ar/H atmosphere over quartz substrates in a two-stage reactor. Approximately 6.5 mol% of ferrocene, which functions as a precursor for producing Fe continuously fed into a tubular quartz reactor. The liquid feed was passed through a capillary tube and preheated to 175ºC prior to its entry into the furnace. At this temperature, the liquid exiting the capillary was immediately volatilized and swept into the reaction zone of the furnace by a flow of argon with 10%.The MWNTs grow perpendicularly from the surface of the quartz reactor tube. After the reaction, the pre-heater and the furnace were allowed to cool to room temperature in flowing.Argon and the MWNT sheets were collected. The resulting MWNTs were characterized by field-emission scanning electron microscopy the collected material consists of highly aligned MWNTs with the dominant tube diameter in the range 20–25 nm with length 20µm.The MWNT clumps were placed in toluene and then sonicated for 30 min to disperse the nanotubes, rinsed with isopropanol alcohol, and then allowed to dry. The nanotubes were then dispersed in a liquid SiO_2 solution (20 wt% SiO2 nanoparticles dispersed in water).The resulting solution was pipette onto the interdigital capacitor of the sensor and dried in room temperature

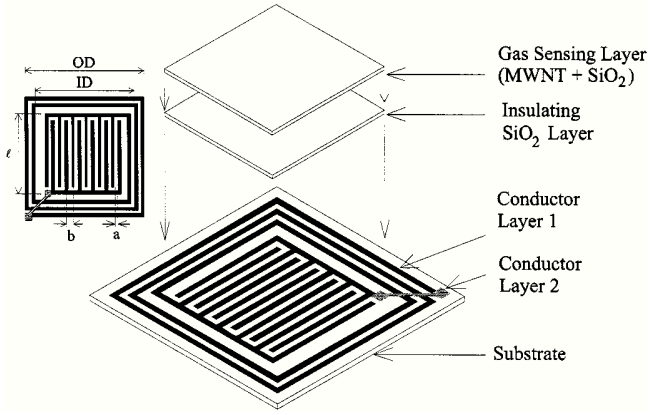

FIG 1. Schematic diagram of a gas sensors

B. Sensor Fabrication

A 2-cm square sensor was fabricated by photolithographically patterning a square spiral inductor and an interdigital capacitor on a printed circuit board (PCB) (Fig. 2).A m thick layer of SiO (confirmed by SEM imaging) followed by an m thick layer of MWNT-SiO mixture were then coated onto the capacitor of the sensor, with a resulting sensor cross section as shown.

C. Sensor design

The general sensor structure is shown in Fig. 1. It consists of a printed inductor-capacitor resonant circuit that is first coated with a protective, electrically insulating SiO layer (see Fig. 2), followed by a second layer of gas-responsive MWNT-SiO2 mixture with the SiO2 matrix acting to physically bind the MWNTs to the sensor. As the sensor is exposed to various gases, the relative permittivity and the conductivity of the MWNTs vary, changing the effective

complex permittivity of the coating and hence the resonant frequency of the sensor.

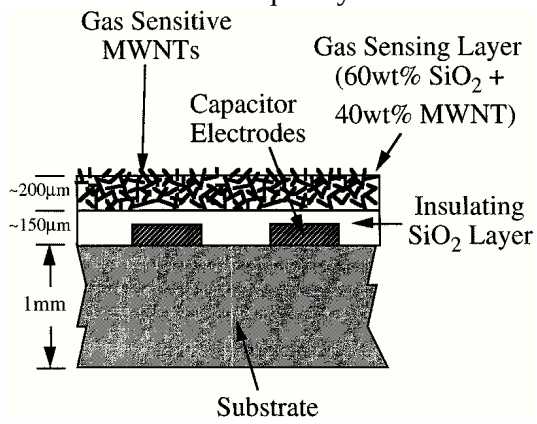

FIG 2 Cross-sectional view of the interdigital capacitor

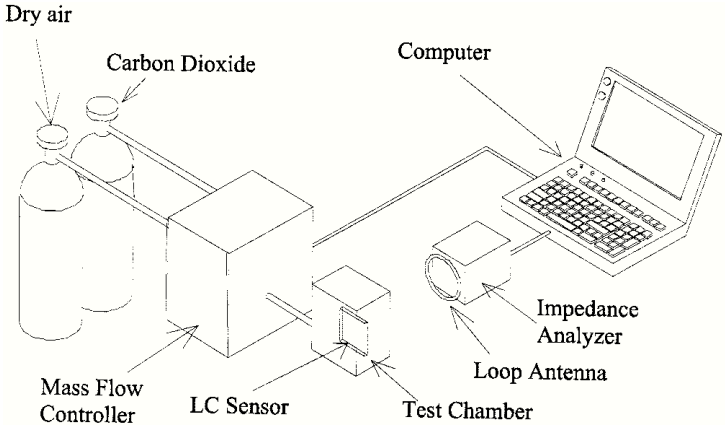

FIG 3 Experimental set up

D.Experimental set up

The testing facility is schematically depicted in Fig. 3. The sensor was placed inside a sealed Plexiglas test chamber and monitored with a single-turn 16 cm diameter loop-antenna located approximately 15 cm from the sensor. Test gas concentration was controlled with a mass flow controller (MKS Instruments multi gas controller). The antenna impedance was measured with an impedance analyzer. A computer was used to control the mass flow controller and the impedance analyzer. After passing the gas from the sensors MWNT permittivity and conductivity were changed and following results were seen

1 sensor response is reversible for oxygen, carbon dioxide, but irreversible for ammonia

2 operational characteristics make sensors attractive for long term wireless monitoring application such as monitoring of environmental ammonia level in an industrial area

3 it was found ϵ_r'' (proportional to conductivity) MWNTS shifts lower when the sensor is exposed to either carbon dioxide or ammonia since it is a reducing agent. While shifts to higher side when exposed to oxygen as it is an oxidizing agent.

Hydrogen gas sensor technology

First, we have fabricated the CMOS IC using the standard 0.35-μm CMOS process. The second post processing step is dipcoating of single walled CNT (swCNT). The swCNTs are sonicated in nitric acid at 50 ◦C for 30 min to purify and simultaneously exfoliate them from bundles. Thereby forming the CNT network (CNN) on the substrate. Since the Al cannot withstand temperatures higher than 500 ◦C, all the post processing steps should be done at the low temperatures. The final process is the Pd decoration on the swCNT to detect hydrogen molecules. Decoration of Pd NPs on swCNT network is performed by a thermal evaporation method followed by 30-min annealing at 450◦C. After all the postprocesses, the CMOS IC is mounted on a printed circuit board. Fig. 4 shows the conceptual diagram of the proposed post-processing step

The first post processing step is electroless plating of gold on the exposed Al surface, requiring no additional photolithography process. Pd nanoparticles (Pd NPs), a catalyst for activation of Au, were deposited by immersing the fabricated CMOS IC into

the solution for Pd activation at room temperature for 3 min, Which is a mixture of 0.8-mL 0.1-g/L $PdCl_2$ solution, 1-mL 85% phosphoric acid 6 mL of methyl gallate, 1 mL of polyethylene glycol, and 7-mL deionized (DI) water at room temperature for 3 min. In this step, Pd catalysts were deposited only on the top of Al metal layer selectively. Thereafter, the solution for Au plating, which is made up of 58.5 mg of KCN, 0.913 g of citric acid, 0.128 g of KAuCN2, 2 mL of hydrazine, and 50-mL DI water, was used to plate Au on the Pd layer
.

The second post processing step is a dipcoating of single walled CNT (swCNT).SwCNTs are sonicated in nitric acid at 50 ◦C for 30 min to purify and simultaneously exfoliate them from bundles. The swCNTs are then neutralized with DI water and trapped on a membrane filter (Millipore, 0.2-μm pore size,47 mm diameter) by using a vacuum filtration method. The swCNTs on the filter are dried in a vacuum oven chamber at 80 ◦C for 48 h. We used 1,2-dichlorobezene (1,2-DCB) as a solvent to make swCNT colloidal solution. The prepared swCNTs are finally solubilized in the 1,2-DCB (0.05 mg/1 mL) by sonication for 10 h. The swCNTs have a diameter of 1–2 nm and a length of several micrometers. The fabricated CMOS IC is immersed into the swCNT colloidal solution. Subsequently, the stage moves downward at a constant speed, and the CMOS IC is pulled out from the solution at 3-mm/min withdrawal velocity, thereby forming the CNT network (CNN) Thus, the CNT dipcoating is a suitable method to build the highly uniform CNN-based sensor cell array at room temperature.

The final process is the Pd decoration on the swCNT to detect hydrogen molecules. Decoration of Pd NPs on swCNT network is performed by a thermal evaporation method followed by 30-min annealing at 450 ◦C. After all the postprocesses, the CMOSIC are mounted on a printed circuit board and wire bonded. The chip surface, excluding the sensor cell array region, is coated with epoxy resin to protect the bonding wire. The CMOS IC has an address-accessible 8 × 8 CNN cell array where the whole chip size is 5 mm × 4 mm. RESET is a control signal to operate the sensor IC, and row/column decoders process the incoming addresses of a sensor cell (ADD0 □ADD5). The output of a sensor cell (SEN_OUT) shares a signal path with other cells in the same row, being transmitted to the output of the chip through the multiplexer (DATA MUX) and buffer (OUT Buffer) circuit. It has an inner electrode [island electrode (IE)] and an outer electrode [enclosing electrode (EE)] that completely encloses the IE. All the sensor cells share the common EE. The IE and EE are electrically connected to the underlying readout circuitry and *V*DD of the CMOS IC, respectively. The readout circuitry measures the change of *R*CNT − *C*CELL (the resistance of the Pd decorated CNN—the 1-pF capacitance of an embedded capacitor) time constant. The sensing operation has two phases, phase I is charging cell capacitor *C*CELL through *R*CNT and phase II Is discharging it through the pull down nMOS transistor. If the SENSE node voltage goes higher than the logic threshold voltage (about *V*DD/2) of level detector, taking the *R*CNT*C*CELL time roughly, the SEN_OUT node voltage goes to *V*DD level through the inverter chain. Then, the high SEN_OUT node voltage turns on the pull down nMOS transistor and consequently pulls the SENSE node voltage down to ground level (phase II), returning to the initial condition again. In this manner, the SENSE and SEN_OUT nodes oscillate; and the period approximately corresponds to the *R*CNT –

*C*CELL time, proportional to the resistance of the sensor. The SEN_OUT signal is connected to D flipflop in DATAMUX, and finally, OUT signal is generated by OUT BUFFER and displayed on oscilloscope. The hydrogen molecules are adsorbed to the Pd NP, lowering the work function of Pd NP. Then, electrons are transferred from the Pd NP to the swCNT, lowering the concentration of n holes in the p-type semiconducting CNTs, thereby decreasing the frequencies of the sensor cells in the array.

Conclusion is

1. the sensor cells under higher concentration of hydrogen show the larger standard deviation.
2. This method is suitable for low cost mass production and is also fully compatible with existing CMOS processes.

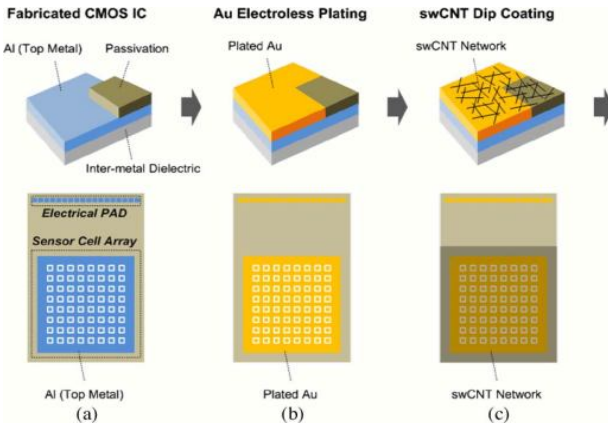

FIG. 4. Sequence of the proposed post processing step. (a) The fabrication of CMOS IC for readout. (b) The electroless plating of Au on the Al surface(c) The swCNT dipcoating. (d) The decoration of Pd NP.

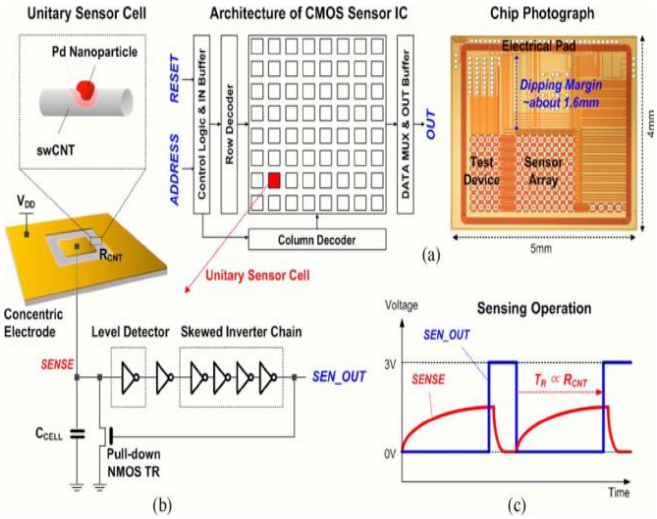

FIG 5. Overall chip architecture and concept of readout. (a) Architecture and its photograph composition of sensor cells.CNN sensor on the concentric electrode and underlying readout circuitry. (C) Timing diagram of sensing

APPLICATION OF GAS SENSORS

Gas sensors are used in many industrial, medical, and commercial applications. For example, oxygen sensors are used in the monitoring of combustion engine environment to increase engine performance and reduce emission of green house gases. Ammonia sensors are important for monitoring ambient ammonia concentration since it is related to many environmental issues such as acidification, human health, and climate change through particle formation. In addition to controlling industrial processes and monitoring air quality, CO sensors are also widely used in food and medicine packages as a means of detecting spoilage.

CONCLUTION

Paper talked about the carbon nanotube and its various properties. Two different approaches were presented for gas sensing. Based on the experimental results, it was proven gas sensing characteristics carried out in this work has shown that carbon nanotubes have potential to be an excellent ammonia and carbon dioxide sensor material at room temperature. The presented method for hydrogen gas sensing is suitable low cost mass production sand is fully compatible with existing CMOS processes. Thus it is expected to have major impact upon the commercialization of CNT technology.

REFFERENCE

1 Development of Carbon Nanotube-Based Sensors—A Review Benjamin Mahar, Cosmin Laslau, *Student Member, IEEE,* Ronnie Yip, and Yu Sun, *Member, IEEE*

2. Carbon Nanotube-Based CMOS Gas Sensor IC: Monolithic Integration of Pd Decorated Carbon

3. Nanotube Network on a CMOS Chip and Its Hydrogen Sensing Sung Min Seo, Jun Ho Cheon, Seok Hyang Kim, Tae June Kang, Jung Woo Ko, In-Young Chung, Yong Hyup Kim, and Young June Park, *Senior Member, IEEE*

4. A Wireless, Passive Carbon Nanotube-Based Gas Sensor Keat Ghee Ong, Kefeng Zeng, and Craig A. Grimes, *Member, IEEE*

5. Carbon Nanotubes: Thermal Properties J. Hone Columbia University, New York, New York, U.S.A.

6. Electronic, thermal and mechanical properties of carbon nanotubes By M. S. Dresselhaus1, G. Dresselhaus, J. C. Charlier and E. Hern´andez

7. Mechanical properties of carbon nanotubes J.-P. Salvetat, J.-M. Bonard, N.H. Thomson, A.J. Kulik, L. Forr´o, W. Benoit, L. Zuppiroli