Catalyst thickness effect on Carbon-Nanotubes diameter and gas response

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***Abstract*— Nanotube based gas sensors are very interested in sensing applications due to their high speed response, selectivity, sensitivity, surface to volume ratio and low-power consumption. In this experiment nanotube multi-walled carbon-nanotube (MWCNT) gas sensor is growth on SiO_2 substrate by Plasma Enhancement Chemical Vapor Deposition (PECVD) method at low temperature and its gas response extracted. For more sensitivity the CNT thickness varied and sensitivity to different gases in different diameter is measured and extracted. Nanotubes diameter changing is done by changing the nickel catalyst thickness. It is observed that increasing the catalyst thickness will increase the nanotube diameter and gas sensitivity, respectively. This incremental procedure has been stopped at a particular thickness and decreases after that. Changing the catalyst thickness from 5 to 20nm results in change of the nanotube diameter from 70 to 150nm. For this thickness variation, sensitivity increases ~50%. The diameter of nanotubes synthesized at each distinct run was calculated based on SEM micrographs of the samples.**

Keywords— Gas sensor, Carbon Nanotube (CNT), catalyst thickness, PECVD.

I. INTRODUCTION

Nowadays sensors play an important role in life and process automations is impossible without them. The demand of sensors with high selectivity and sensitivity, low power consumption and cost cause a progress to new sensor generations. In gas sensor field, nanometer structures based on carbon such as carbon nanotubes make gas detection in room temperature possible. That is because of smaller material size and high surface area. Therefore, sensitivity and response time of gas sensing will improve [1].

Discovering new carbon structures known as fullerenes in 1985, revolutionized the basic sciences and engineering. Fullerenes molecules with SP^2 structure and consists of 60 carbon atoms, are such as a soccer ball.

There are different forms of fullerene. One of its forms drawn around axis, is called CNT. The molecules discovered and produced the first in 1991 [2]. The special and useful properties of these molecules are high conducting and semiconducting property [3, 4], high surface resistance and tension [5], capability of storing gases such as argon and hydrogen [6] and suitable electrostatic property for the production of super capacitors with high capacity [7]. The above mentioned characteristics will make a progress in various industries such as petroleum, oil electronic, communication and etc. which results in saving time and costs.

Nano tubes growth are done in various method. The most common methods are: 1- Electric arc discharge, 2- Laser ablation and 3- Chemical Vapor Deposition (CVD).

In CVD growth the object is going to be coated is placed in contact with the chemical vapor. The first layer of molecules or atoms may react with the surface or not. Any way these deposited new formed samples will act as a surface which the materials will grow on it. The new formed structures from these materials are often placed side by side in a line, because the path which atoms and molecules that have been deposited are affected by nearby molecules or atoms. If the surface or base of deposition host surface is completely flat, the surface growth will do in best way. In deposition, a place for crystallization may be formed along the deposition axis, so that the structure grows vertically on a regular basis and in a line.

CNTs production involves two basic steps: First, catalyst production. Second, production process. In first step will distribute the metal catalyst in a basic material. After catalyst extractions chemical vapor deposition method used in the second step. Usually a catalyst prepared and the set will place in a cylindrical furnace. Then, in the presence of noble gas, furnace temperature increase as much as desired. By cutting off the flow of noble gas, hydrogen gas with specified flow and desired time, stream in the reactor for the synthesis of carbon nanotubes on the catalyst. After required time, the flow of hydrocarbon gas will cut off and noble gas flow is restored. The furnace cools to room temperature. This process usually leads to simultaneous production of single walled and multiwalled carbon nanotubes [8].

The problem with CVD method is high temperature. Plasma method is used to solve it by increase the chemical reaction rate. PECVD method will produce the deposition in lower temperature which is necessary in semiconductor industries, to create an appropriate product. Temperature of CVD with plasma enhancement method is typically lower than thermal CVD growth [9].

Researches shows the CNTs are sensitive to low density of some gases because of small particle size [10]. Therefore carbon nanotubes are widely used in chemical gas sensors [11]. The carbon nanotubes use in gas sensors are due to their hollow and high surface area. CNT contact area with gases is central hollow section and outer wall. Higher the contact surface, increases physical-chemical adsorption of gases on the surface of the nanotube. Since the electronic properties of nanotubes are strongly dependent on their atomic structure, the mechanical structure change [12] or chemical concentration of

them make a great influence in changing their electrical conductivity [10].
Recent studies have shown that CNTs as gas sensors can detect different gases like NH_3 [13, 14], NO_2 [15], H_2 [16-18], H_2O [19], O_2 [18], CH_4 [20] at temperatures lower than 200 ° C and even at room temperature. This reduces the power consumption of the sensor. For detecting flammable gases or exploding gas (e.g. hydrogen), lower working temperature sensor is required.
There are reports about single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) gas sensors. Multi-walled nanotubes due to low cost and high production capabilities are more suitable for use in gas sensors in compare with single-walled nanotubes [20].
Changing the nanotube diameter results in changing Adsorption energy (Ea) and charge transfer (Q), sequentially [11, 21, and 22]. Also, according to many reports from CNT density effects on hybrid samples sensitivity [23-26], we expect that the nanotube diameter change has an effective influence on sensitivity of this samples.
In this experiment the growth method in [27] is used. In this method nanotubes growth in lower temperature, about 350°C. Then with changing thickness of nickel catalyst, diameter of CNT nanotubes vary. This changes result in variations in sensitivity range.

II. EXPRIMENTAL

A. *CNT growth*

In most of CNT growth method, temperature is high about 650C. This make substrates such as silica which has high melting temperature a suitable for nanotube growth. But using silicon because of high prices is economically not appropriate. Therefore lower temperature methods are preferred. There are many ways for carbon nanotubes growth at low temperatures, such as using a second catalyst [28], the use of two furnaces [29] or the use of microwaves [29].
Low temperature growth of carbon nanotubes using PECVD, the way two zonal furnaces (temperature zone) is used. As mentioned in section1, multiwalled CNT is preferred. A direct plasma and distant method was used to grow aligned MWCNTs. This method is known as low temperature [27]. For this approach, glass substrate which nickel is deposited placed on the second zone (lower temperature). At the beginning temperature is 300˚C and at growth phase is 400 ˚C. The plasma environment, directed the growth mechanism and growth may occur in the same direction with the electrical field. In order to reduce the temperature to 300-400 degrees, two zones plasma is used which the electric field intensity and temperature of 700 ° environment, leads to the breakdown of carbon-carbon bond acetylene gas as a carbon source. Free radicals produced in this zone with gas flow entering the system, push them to the second zone. Mean free path length of radicals let the space from Zone 1 to Zone 2 up to 20 cm change. Because the temperature in the furnace temperature is gradient to 300 degrees, it can be said that the temperature in the zone of 2 is about 300 to 400 degrees. Zone 2 has plasma environment similar to Zone 1 except that for directional growth, plasma dc is used in this environment. Therefore, we are be able to grow nanotubes at temperatures between 300 and 400 degrees.
Potential difference between plates of zone 1 and 2 make the DC plasma. The decomposed electrons and ions of atoms by plasma with direction of electrical field cause the vertically growth of Multi-walled CNT.
Nickel on substrate is a catalyst. The thickness of nickel layer is 5-20 nm. Nickel is deposited by sputtering. To use this technique Acetylene (C2H2) and hydrogen (H2) gases are introduced.

Process of carbon nanotubes growth is very sensitive and requires careful control and also our purpose is growth aligned at low temperatures. Figure 1 shows Schematic of PECVD system for vertical growth of carbon nanotubes.
CNT growth involves three steps: 1- annealing, 2- hydrogen plasma, 3- Acetylene plasma. In period of annealing the substrate is heated for 12 minutes. Then H_2 gas flow rate of 60sccm apply in this temperature for 5 min. Hydrogen plasma is formed so Nano islands of Ni crated. In this step plasma power was set 4.5W/cm2. This power is controlled DC voltage adjustment. The Steps to a pretreatment for CNT growth that marks the morphology of carbon nanotubes. Then acetylene gas is applied at a flow rate of 10sccm for 20 min. in this step plasma power is 6W/cm2. After this time acetylene gas flow is interrupted, while H2 gas is introduced to chamber, PECVD system cooled. The scanning electron microscopy (SEM) in Figure 2 and it's characterized shows the aligned morphology of MWCNT.

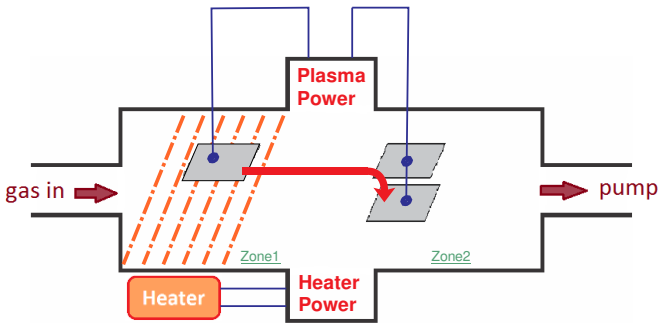


Fig. 1. Block diagram of PECVD system and mechanism.

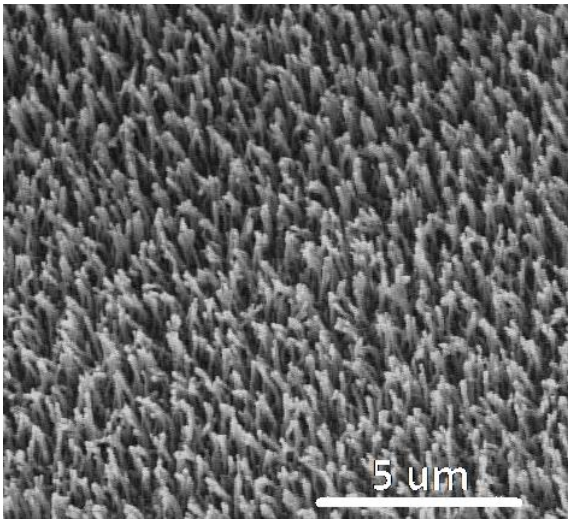


Fig. 2. SEM micrograph of CNT.

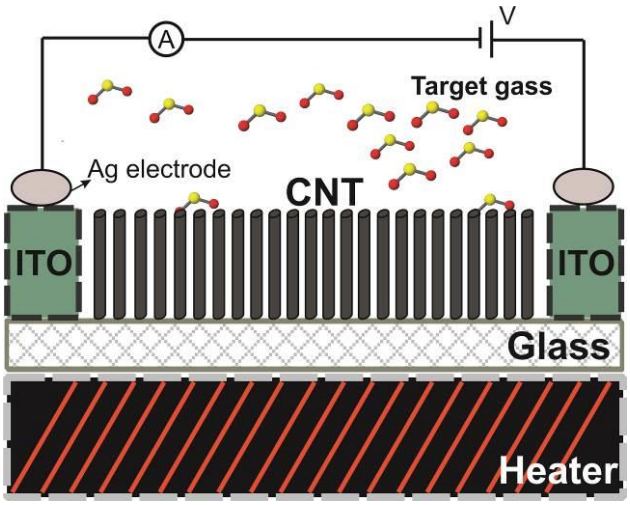


Fig. 3. The schematic diagram of fabricated CNT samples.

B. Measurment methods and response record

For electrical contact, Ag electrode and ITO deposition with sputtering is used. The ITO thickness is set 150nm. Because of heater the Ag will melt so the platinum used as contact. Fig. 3. Shows the measurement and response record system of this experiment. For sensitivity (1) is used.

$$S = \frac{Rb-Rg}{Rb} \times 100 \quad (1)$$

Which Rb is resistance of two ends of terminal after gas exposure. Rg is exact resistance after stability.

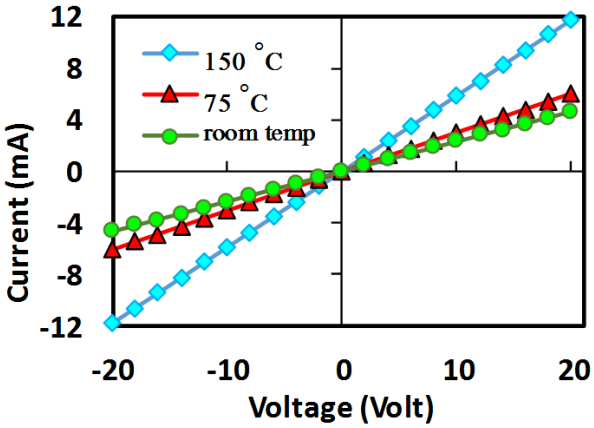


Fig. 4. I-V characteristic of CNT sample.

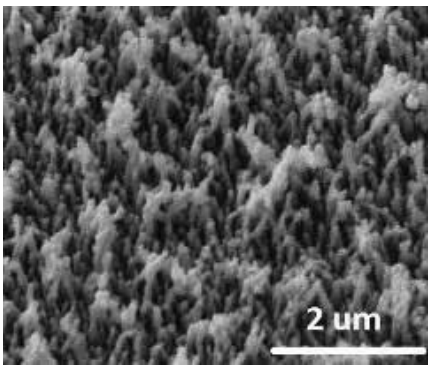
III. Results and Discution

For measurement and test of CNT sample the test circuit of Fig. 3. Is used. The Ag electrodes at the top of ITO contact are installed. By a micro-Heater exact temperature will be set for each sample.

The I-V curve of CNT sample at different temperature is obtained. As in Fig. 4 illustrates, Ag-CNT contact shows ohmic behavior.

For improve the effect of nanotube diameter on sensitivity, different thickness of nickel deposited. These catalysts are used for CNT growth. The SEM shown in Fig. 5 illustrates that changing the nickel thickness will affect the nanotube diameter. The chart in Fig. 6 shows the effect of increasing the nickel thickness on nanotube's diameter in a wider range.

The samples exposure by 4000ppm butanol gas in room temperature for sensitivity test. As Fig. 7 illustrates, increment the diameter of CNT nanotubes in three different samples with diameter less than 120nm results in increment the sensitivity about 50% and then sensitivity slowly decreases. These changes are well shown in Fig. 8.



(a)

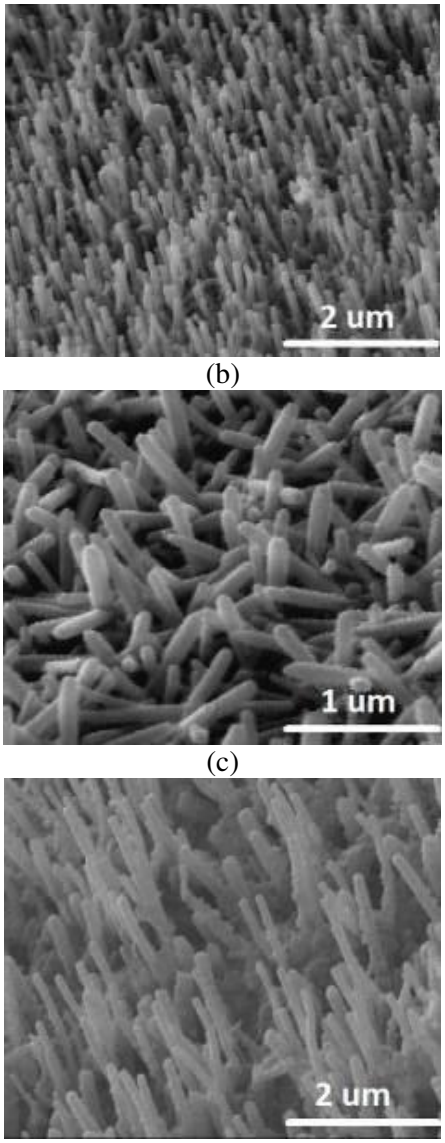


Fig. 5. SEM graph of the CNT samples. (a) Sample 1: nickel thickness 5nm, nanotube diameter 70nm. (b) Sample 2: nickel thickness 10nm, nanotube diameter 105nm. (c) Sample 3: nickel thickness 15nm, nanotube diameter 125nm. (d) Sample 4: nickel thickness 20nm, nanotube diameter 145nm.

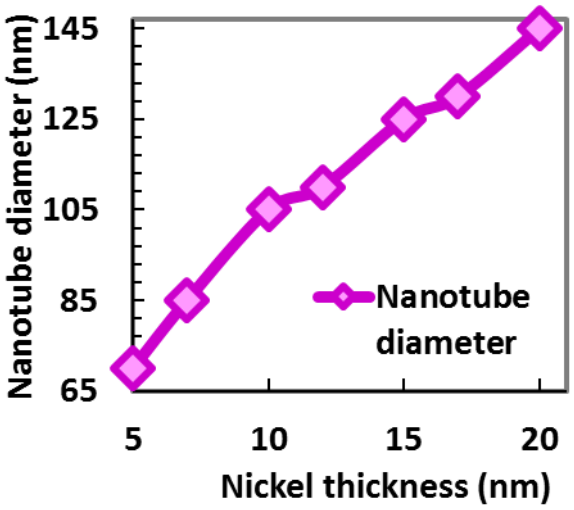


Fig. 6. SEM graph of the CNT samples.

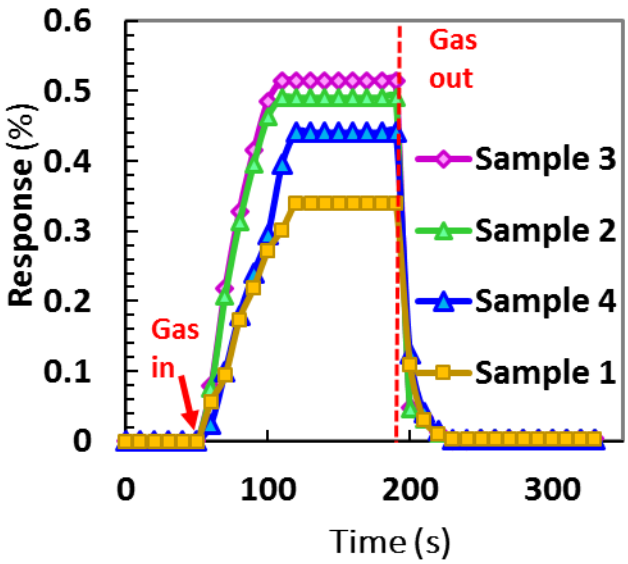


Fig. 7. Response of the CNT sample gas sensor in 4000ppm concentration of butanol at operation room temperature. (The sample name is according to number of SEM's, Fig. 5)

It is obvious from Fig. 8 the more nanotube diameters increase, due to higher contact surface for gas molecules, CNT nanotubes response and sensitivity increase. When nanotube diameter increase from ~125nm and more, increasing the nanotube diameter, results in reduction of surface to volume ratio. This is because of CNT nanotube compaction which decrease the sensitivity.

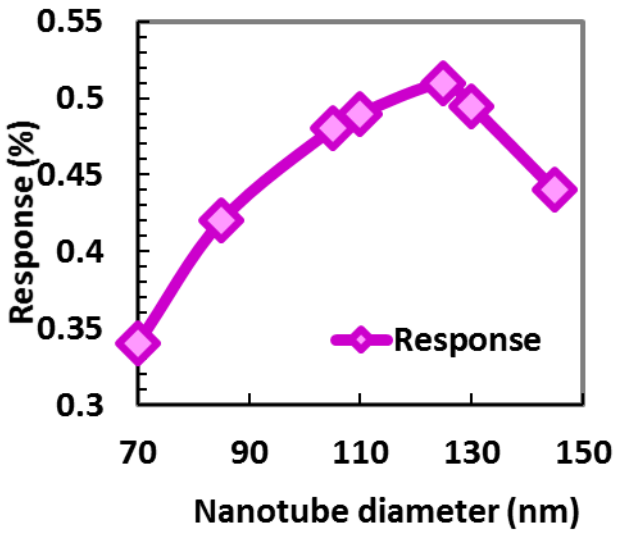


Fig. 8. SEM graph of the CNT samples.

For more investigation around the experimental results the lifetime of each sample is evaluated. In this evaluation criterion of lifetime is unpredictable changes of sensitivity into the specific gas at different time and periods. It has been realized that the nanotubes samples with higher diameter has more lifetime. Table 1 shows lifetime of samples.

TABLE I. CHARACTERISTIC LIFETIME CNT SAMPLES.

	Samples			
	Sample 1	***Sample 2***	***Sample 3***	***Sample 4***
Nickel thickness (nm)	5	10	15	20
Nanotube diameter (nm)	70	105	125	145
Lifetime (months)	2	5	5	6

IV. CONCLUSION

We has successfully realized that change in nickel catalyst thickness has effect on CNT growth in PECVD method results in changing the diameter of growth nanotubes. This change in diameter of nanotubes has results on contact surface of CNT samples and butanol gas molecules. Therefore improve the response of growth CNT gas sensor to specific gases.
Also, it is clearly shown that lifetime of growth samples with higher diameter is more than samples with smaller diameter.

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