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PREPARATION OF CARBON NANOTUBE GAS SENSORS BY INKJET PRINTING PROCESS FOR MONITORING OF POLLUTANT NO_X GAS IN AIR

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ABSTRACT
Single walled carbon nanotube (SWCNTs) gas sensors were prepared by inkjet printing process to deposit controlled less amount of SWCNTs on the substrate in a designed pattern with a view to have higher sensitivity and response time and to produce a large amount of sensor for air pollution monitoring. SWCNTs solution was prepared by mixing with pure water and SDS (sodium dodecyl sulphate)) and this solution was used an ink for the inkjet printing. The method works by ejecting SWCNTs as an ink on the silicon substrate through very fine nozzles to prepare sensor. The sensor surface was characterized by Scanning Electron Microscopy (SEM) and Raman spectroscopy. The sensitivity of the sensors was measured using change of electrical conductance by exposing to different concentrations of NO_2 gases. The resistance of the sensor was found to be decreased with increasing gas concentration**.** Sensors containing less dense SWCNTs showed higher sensitivity compared to the denser SWCNTs

Keywords: Carbon Nanotube, Inkjet Printing, Air Pollution, Gas Sensor, Monitoring, Nox Gas.

1. INTRODUCTION

Carbon nanotubes (CNTs) are attractive potential materials for nanotechnology application because of their exceptional electronic properties and mechanical strength. Since their discovery in 1991 by Iijima [1], carbon nanotubes (CNTs) have attracted the scientific interest due to their unique structure and promising properties that make them potentially useful for applications including nanoelectronics, multifunctional composite materials, or field emission devices [2]. CNTs are hexagonal networks of carbon atoms that can essentially be thought of as a layer of graphite rolled-up into a cylinder. Depending on the arrangement of their graphene cylinders, there are two types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). SWNTs have only one single layer of graphene cylinder, while MWNTs have several concentric layers. Their high specific surface area (>1500 m^2/g), high aspect ratio, size, and hollow geometry also make them promising candidates for their use as components of gas and chemical sensors. As a result of their remarkable physical and structural properties, CNTs are good candidates to be utilized as components of sensors with improved real-time monitoring of combustible gas alarms, gas leak detection, and environmental pollution monitoring, etc. SWNTs and MWNTs as sensitive materials for the detection of gases such as H_2, NH_3, NO_2 or O_2 have already been successfully demonstrated [3-7].

The emission of nitrogen oxides (NO_x, NO and NO_2) due to the high temperature gas combustion (vehicles, electricity generation, and industrial processes) results in both smog and acid precipitation, and affect both terrestrial and aquatic ecosystems. Nitrogen monoxide is unstable and quickly forms NO_2, which is an oxidizing gas that is present in all urban atmospheres. NO_2 is a brownish, highly reactive gas and a deadly poison by inhalation. The NO_2 gas detection has normally been carried out by chemiluminescence or non-dispersive infrared analysis [8-9]. These traditional methods employ large and expensive instruments and require sampling systems as well as complicated maintenance. Therefore, an effective method to monitor NO_2 is demanded for atmospheric environmental measurement and control. Research has been focused on the development of sensors capable of monitoring low NO_2 concentrations.

Functional materials such as polymers or biomolecules are most suitably processed from solution. In this respect, inkjet printing is a particularly attractive technique especially for the controlled solution deposition of small quantities of functional materials in conformity with specific patterns [10]. The technique operates ejecting single drops of an ink through very fine nozzles (with a 20–100 μm in diameter), at ambient temperature and with no contact or vacuum [11-12]. The only constraint is the requirement to have fluids with suitable viscosity (lower than 20 cP) and surface tension (in the range 28–350 mN m^{-1}). Important parameters are the ink jet nozzle, the substrate, viscosity and surface tension of printing liquid.

The advantages of ink-jet printing compared with other techniques to deposit thin layers of polymer films onto a variety of solid substrates, such as

electrochemical deposition [13], thermal evaporation [14], spin coating [15], dipping coating [16], photolithography [17], lie in its pattering capability, in the efficient use of material and the low cost of the process, in the compatibility with a wide range of substrates and, finally, in the high level of technical development. Many inkjet applications are now emerging through both patents and scientific literatures in several fields. Recently, different groups have investigated the possibility to use ink-jet technique for chemical sensor applications[18-21], mainly using conducting polymers such as polyaniline as the sensing film. The most advantage of the ink-jet-printed films is a series of partially overlapped droplets that allows rapid diffusion of the vapour molecules into and out of the film, leading to sensor fast response and improved recovery times [22].

CNTs aggregate during preparation and have difficulty in placing controlled small amount of CNTs with high precision in micro or nano electronic device structures. So, inkjet printing process is very effective for fixing a very small amount as a designed pattern on the wafer for gas sensing application. In this work, SWCNTs gas sensors have been prepared for environmental applications especially for the NOx gas detection.

2. EXPERIMENTAL DETAILS

In this experiment, the inkjet nozzle was used to deposit SWCNTs solution on the Pd prefabricated interdigitated electrodes (called as the sensor substrate) and also on the silicon wafer. The position of the inkjet nozzle was fixed and the sensor substrate was placed on the X-Y stage. The X-Y stage was moved during printing controlled by using a PC to draw designed pattern of SWCNTs dotted line on the sensor substrate. SWCNTs prepared by pulsed laser ablation (PLA) method and commercially available SWCNTs prepared by direct injection pyrolytic synthesis (DIPS) were used in this experiment. At first, different concentration of SWCNTs solutions were prepared by dispersing in 1 wt. % SDS (sodium dodecyl sulphate) adding with pure water. To unbundle SWCNTs and to prepare a homogeneous SWCNTs solution, it was properly ultrasonicated by an ultrasonic homogenizer. Theses homogeneous SWCNTs solutions were used as an ink to print SWCNTs on the sensor substrate by using inkjet nozzle. The ratio of SWCNTs ink to pure water in three different solutions was 1:100, 1:30, 1:10. The amount of the SWCNTs on the substrate was controlled by the number of inkjet dots per length. The distance between adjacent droplets was controlled by controlling the moving speed of the X-Y stage. Table 1 shows the preparation condition for printing SWCNTs on the silicon substrate for preparing gas sensor. A CCD camera was used to adjust the droplets intervals. One single line of SWCNTs of 5 mm length using different contraptions of SWCNTs solutions was printed on the silicon substrate for single or several times scanning. Figure 1 shows the view of single line of SWCNTs printed by the inkjet printer on the silicon substrate. After printing SWCNTs on the silicon substrate, SDS was removed from the sensor substrate by rinse in pure water for 10 minutes to measure the sensitivity. .

Table 1: Preparation condition

Inkjet parameters	Value
Nozzle diameter	90 µm
1st Pulse length	50 µs
Pause	10 µs
2nd pulse length	20 µs
Frequency of	20 Hz
Temperature	Room temperature
X-Y stage speed	500-200µm/s

After removing SDS from the SWCNTs line on the Si substrate, silver paste was put at the both ends of the line to form the two terminals. Thin copper wires were connected at the two terminals of the SWCNTs line for measuring electrical conductance by exposing to different concentration of NO_2 gas.

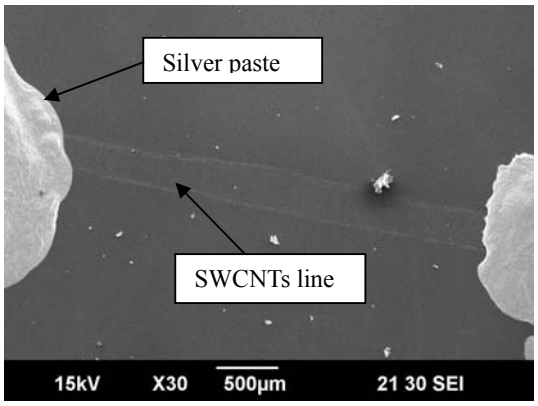

Fig 1. View of single SWCNTs line on silicon substrate printed by inkjet printing for a gas sensor.

3. CHARACTERIZATION OF SAMPLES

The sensor surface was characterized by Scanning Electron Microscopy (SEM) and Raman spectroscopy. Raman spectroscopy is a simple and useful technique to characterize the quality of the carbon nanotubes. The Raman spectra were measured using a micro Raman system (Princeton Instrument CCD and a diode laser of 532 nm in wavelength). The results examined for the SWCNTs are shown in Fig.2. The Raman spectra of carbon nanotubes typically consist of two major peaks at $\sim$1340 cm^{-1} and $\sim$1590 cm^{-1}, or the so-called D- and G-bands, respectively. The D-band is known to be associated with defective, disordered graphite or glassy carbon, while the G-band is related to the sp^2 vibration of a two-dimensional hexagonal lattice in the graphite. The high G-band with respect to the D-band is a typical feature of the SWCNTs having high crystalline quality. The small D-band peak indicates that the film contains small but finite amount of amorphous carbon (and

defects). The SWCNTs show the vibration peaks of the radial breathing mode (RBM) in the range of 100–300 cm^{-1}, which are related to the diameters of the nanotubes.

Fig. 3 shows the SEM image of SWCNTs gas sensing line with concentration ratio of SWCNTs ink to water of 1:30. Figures 4, 5 and 6 show the SEM top-view

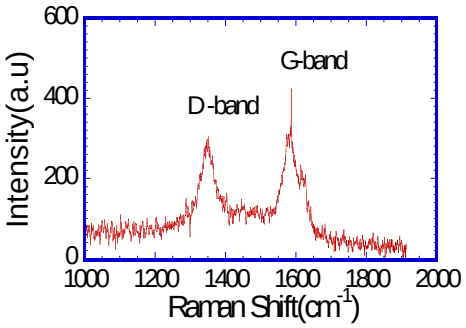

Fig.2. Raman Spectra of SWCNTs used in the gas sensor.

images of the SWCNTs line with concentration ratio of 1:10 at three different positions (at the middle, at the edge and at between middle and edge) on the printed line grown on the silicon substrate for the gas sensor. At the middle position, number of SWCNTs appears to be less compare to the edges. The carbon nanostructures are clearly characterized as a tangled net with a film thickness of 150–250 nm and a diameter of the mats of nanotubules in the range of 10–20 nm. The aspect ratio of the CNTs layer was estimated in the range of ...

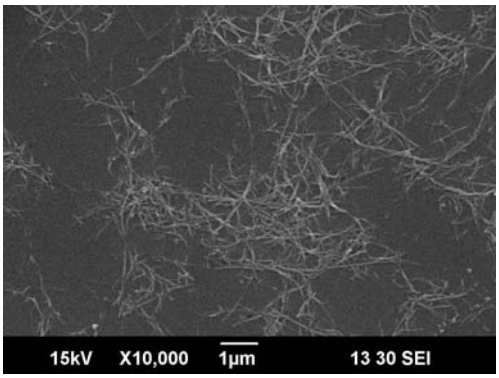

Fig.3. SEM view of SWCNTs line printed on Si substrate (CNTs:water=1:30)

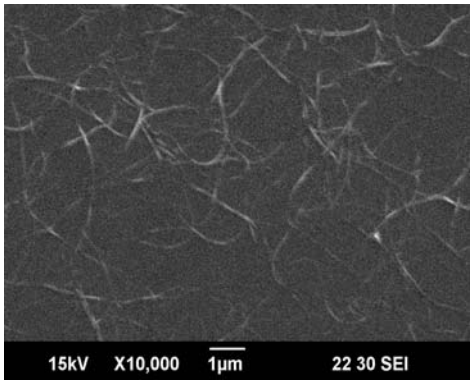

Fig.4.1. SEM view (middle of line)of SWCNTs line printed on Si substrate (CNTs: water=1:10)

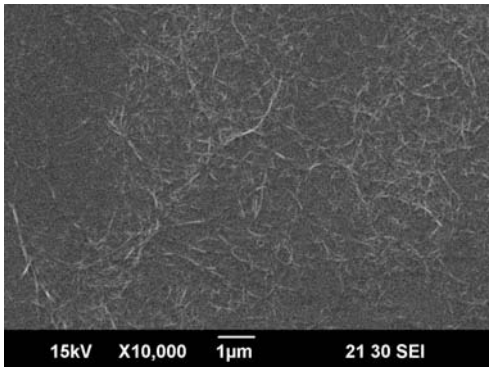

Fig.4.2. SEM view (between edge and

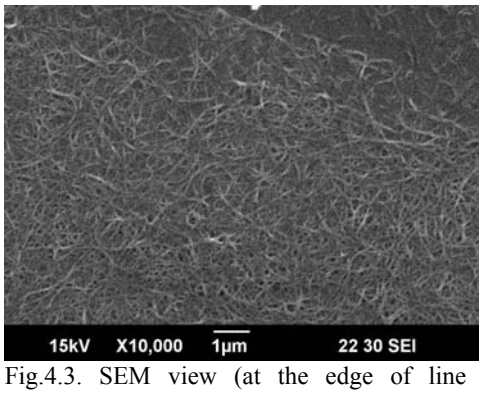

Fig.4.3. SEM view (at the edge of line)of SWCNTs line printed on Si substrate (CNTs: water=1:10)

4. RESULTS AND DISCUSSION

The sensitivity of the sensors were measured by exposing to different concentrations of NO_2 gas. The sensitivity was measured based on change in electrical resistance of the sensor due to exposure to the target gases using the following equation. Sensitivity, S is defined as

$$S = \frac{R - R0}{R0} \times 100\,\% \qquad (1)$$

, where R is the resistance of the sensor in the NO or NO_2 gas and R_0 is the resistance of the sensor in air or N_2 gas. The prepared SWCNTs sensor was annealed in air for three hours, at 150°C to stabilize its gas sensing characteristics. The two terminals of the sensor electrodes were contacted with thin copper wire using silver paste to connect with sensor measurement circuit of the chamber. The resistance of the sensor was found to be decreased with increasing NO and NO_2 gas concentration**.** For gas sensing, the sensor was loaded in a chamber shown elsewhere [23] and then N_2 was purged for 2 hours to stabilize a base measurement line. The gas responses were performed at different temperatures and also at room temperature. The sensing measurements were done for 10 -30 min exposure to gas followed by a 10 min recovery period in pure N_2 gas. Figs. 5 and 6 show the response for 10 ppm NO_2 gas of the sensors, where the 10 and 2 SWNTs lines were overwritten using SWCNTs solution (1:30), respectively. For the both sensors, resistance values were in the kΩ range and it was higher for single scanning compared to 10 times scanning. For 2 times scanning, the response was unstable compared to 10 times scanning. For 1 time scanning it showed no response to 10 ppm NO_2 gas which is not shown here. It showed that the gas sensor is sensitive to NO_2 gas exposure at concentration of ppm level at room temperature and atmospheric pressure. The mechanism of SWCNTs gas sensor is that SWCNTs work as p-type semiconductor and when it absorbs oxidizing gas, their electric conductance is modified by the electron transfer from SWCNTs to absorbed molecules.

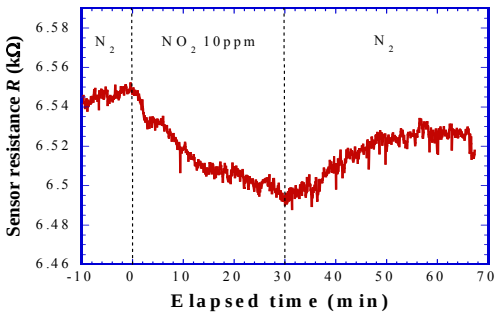

Fig.5. SWCNTs line gas sensor (ratio 1/30 and 10 times scanning) response to10 ppm NO_2 gas at room temperature.

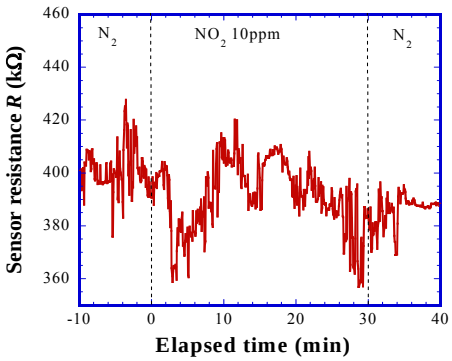

Fig.6. SWCNTs gas sensor (ratio 1:30 and 2 times scanning) response to 10 ppm NO_2 gas at room temperature

Figs.7 and 8 show response of the SWCNTs sensors at room temperature, where SWCNTs lines were put line for 1 and 2 times scanning, respectively using CNT ink (ratio 1:10). For 1 time scanning, the response was not good but for 2 times scanning the response was good to NO_2 gas.

Fig.8 showed that the detection level of sensors was reached to 1 ppm NO_2 with uniform performances at room temperature and atmospheric pressure. The sensitivity was obtained to be 5.0% for 1 ppm NO_2 and it was decreased to 4% and 3% for increasing the

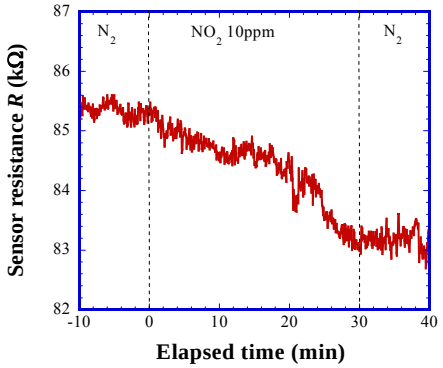

Fig.7.SWCNTs sensor (ratio 1/10 and 1 time scanning) response to 10 ppm NO_2 gas at room temperature and atmospheric pressure.

concentration to 5 ppm and 10 ppm respectively. The electrical resistance of the films decreases with increase in the number of absorbed molecule. Inkjet printing method controls the density of SWCNTs on the substrate and may result in control of resistances. Sensors containing less dense SWCNTs showed higher sensitivity compared to the denser SWCNTs. Detecting target gas at atmospheric condition is an advantage in sensor operation and fabrication as well by simplifying the structures. It applies that the controlling exposing surface area by partially overlapping the droplets of

SWCNTs by inkjet printing process may accelerate the reaction to molecules to improve response time and sensitivity without heating or vacuum. From the above results, SWCNTs sensor prepared with ratio of 1:10 SWCNTS with 2 times scanning single line is the best out of other sensors prepared with other ratios and scanning times .

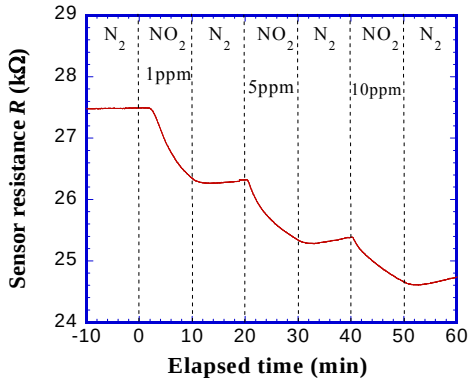

Fig.8. SWCNTs gas sensor (ratio 1:10 and 2 times scanning) response to 1-10 ppm NO_2 gas at room temperature.

5. CONCLUSION

SWCNTs gas sensors were prepared by inkjet printing method successfully for air pollutant NOx gas monitoring. SEM measurement showed presence of carbon nanotube on the sensor prepared by inkjet printing process. Raman Spectroscopy also confirmed SWCNTs by measuring spectra in the RBM range. From electrical measurement of resistance, i.e., the conductivity, response to NO_2 gas was confirmed. By this method it is possible to fabricate a large amount of gas sensors in a short time with high efficiency. This method is effective to deposit small amount of CNTs at atmospheric pressure and temperature in a designed pattern to fabricate gas sensor with improved sensitivity and response time. SWCNTs sensor prepared with ink CNT ratio of 1:10 with 2 times scanning showed the best performance out of other sensors prepared in this experiment. It has advantages to print droplet of SWCNTs with partial overlapping which may improve the conductance and response time. The prepared sensors showed a response in the range of ppm level of NO_2 gas and it can be apply for detection of NOx gas in air at room temperature. By controlling the amount of SWCNTs further and by removing the metallic or graphite property from the SWCNTs it may be possible to detect NOx gas in the range of 100 ppb or less with faster response and recovery time.

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7. NOMENCLATURE

Symbol	Meaning	Unit
R	Resistance	Ohm

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