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Characterization of Aligned MWCNTs Array as the Sensing Element for Ionization Gas Sensor

[1]A.R. Kermany, [2]N.M. Mohamed and [2]B. Singh
[1]Electrical and Electronics Engineering,
[2]Department of Fundamental and Applied Sciences, University Teknologi PETRONAS,
Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

Abstract: Studies on gas sensor technology have intensified with the increasing demand in many fields which require high safety standard. In order to realize this aspect of utilization, gas sensors with improved sensitivity, selectivity and fast response time are critically needed to be developed. With the discovery of carbon nanotubes (CNTs), development is now focused towards CNT-based sensors because of their inherent properties such as small size, high strength, high electrical conductivity, low voltage operation, good stability, long lifetime and large surface area. CNTs are used as the active component in gas sensors. With ionization mechanism, the gas is sensed by measuring its unique electric field breakdown voltage. The non-aligned CNT has been tested as the gas sensing element, but there is still a critical need to produce and test vertically aligned CNTs, since they result in a higher electric field and lower breakdown voltage, producing a more efficient gas sensing device. The objective of the research is to improve the performance of the ionization-based gas sensor using aligned carbon nanotubes array. Testing has been done using different equipments to check the characteristics of the Multi-Walled CNT (MWCNT) sample in comparison with the non-aligned CNTs which was previously designed.

Key words: Gas sensor, ionization mechanism, aligned MWCNT, characterization

INTRODUCTION

A sensor is a device, which detects an input quantity and converts it into an electrical or optical signal which can be read by an instrument. Gas sensors operate by different mechanisms and they are mainly classified into two modes of operation; chemical type gas sensors operating by gas adsorption, and physical type ionization-based gas sensors (Sinha *et al.*, 2006).

The chemical type sensors operate by measuring the changes in the resistance before and after the gas exposure. This method is limited to single type gases and has low selectivity (Cho *et al.*, 2005; Moon *et al.*, 2003).

Gas ionization takes place between two plates (cathode and anode) within a small distance apart which is connected to a high voltage power supply (Modi *et al.*, 2003). Using this method, breakdown voltage of each gas will be measured which is due to the regeneration of secondary electrons under sufficient electric field. This method has a very good selectivity compared with the conductivity-based sensors since every gas has a unique breakdown voltage, which can be used as a fingerprint for gas identification (Pham, 2003; Huang *et al.*, 2009). Current gas sensors are made using semiconducting oxides (ZnO and SnO_2) as their sensing material. Semiconducting-oxide sensors performance is excellent, but they still have some drawback such as limitation on their size. Especially after the introduction of nanotechnology, miniaturized sensors have become a notable interest since they will lead to lower power consumption and cost (Sinha *et al.*, 2006).

In order to overcome the stated problems, new materials are being investigated for gas sensing applications, one of which is carbon nanotubes (CNTs). CNTs were first found by Iijima (1991) and have been applied in different fields after their discovery.

Intense research have been carried out in order to realize the possibility of developing gas sensor with improved sensitivity, high selectivity and fast response time by using CNTs.

CNTs are divided into two types, namely single-walled CNTs (SWCNT) and multi-walled CNTs (MWCNT). A SWCNT is a graphite sheet that is rolled into a cylinder of a few micrometers in length and a few nanometers in diameter. A MWCNT consists of several such cylinders nested inside each other (Ciraci *et al.*, 2004).

Corresponding Author: A.R. Kermany, Electrical and Electronics Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

CNTs are being sought after as the sensing element in gas sensor because of their remarkable mechanical properties and unique electronic properties as well as the high thermal and chemical stability and excellent heat conduction (De Jonge, 2004; Wang and Yeow, 2009). CNT based gas sensors are able to generate very high electric fields at relatively low voltage, thus lowering the breakdown voltage (Liu *et al.*, 2009; Wu *et al.*, 2008).

The behavior relating to the electronic property of CNTs being a strong function of their atomic structure and deformations will make them useful when developing minute sensors that are sensitive to the chemical and physical environment.

The objective of this research is to study the structural and electrical characterization of aligned MWCNTs array that will be used as the sensing element for the ionization gas sensor. Measurements such as current-voltage (IV), conductivity, and resistivity are used to identify how nanotubes behave in a nanotube-based sensor. The electrical data obtained will be compared to the carpet-like array of MWCNTs used in the previous study done by Thaha (2008).

MATERIALS AND METHODS

Highly oriented MWCNTs array was synthesized by catalytic chemical deposition method using Aluminum (Al) as catalyst and Iron (Fe) as buffer layer (Lai *et al.*, 2008). The as-produced MWCNTs array was then analyzed by FESEM with EDX, TEM, XRD and Raman Spectroscopy. A Hall Effect measurement technique was carried out to determine the carrier type, resistivity and conductivity of the sample. As these procedures will help in characterizing the sample and the obtained results will be used for the purpose of comparison with non-aligned MWCNTs.

RESULTS AND DISCUSSION

Sample properties were found using characterization, two stages of characterization was done namely, Structural characterization and Electrical characterization, in order to obtain the required properties.

Structural characterization: Different equipments and methods were used to find the structural characterization of the MWCNT sample. Some of which are Field Emission Scanning Electron Microscopy (FESEM), Energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Raman microscopy.

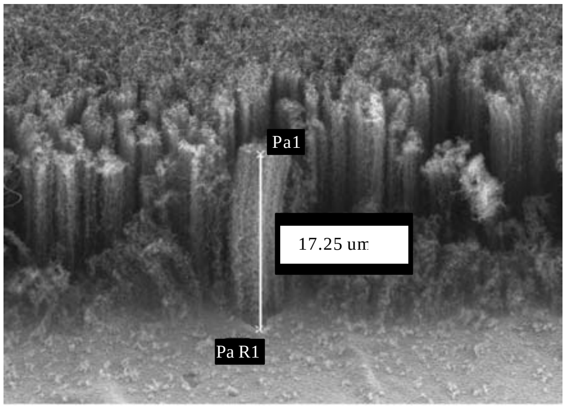

Fig. 1: Highly oriented MWCNT array with 17.25 (um) height

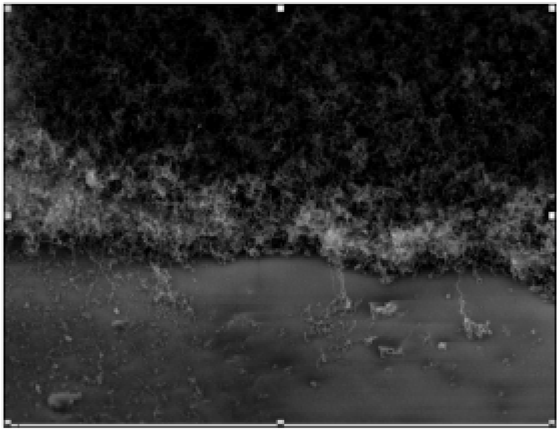

Fig. 2: Non-aligned multi-walled carbon nanotubes

Figure 1 shows the FESEM result for two highly oriented CNTs with different lengths. Using FESEM; the topography, morphology, heights and straightness of the sample were observed. Shorter length will result in a shorter conductive path and so lower breakdown voltage.

For the purpose of comparison a CNT sample, produced by Thaha (2008), FESEM result is shown in Fig. 2. It can be seen that the MWCNT sample in Fig. 2 is not vertically aligned and it has a carpet-like shape which has a longer conductive path compared to the samples shown in Fig. 1.

EDX analysis is used for identifying the elemental composition of the CNT. As it can be obtained from Table 1, the sample is made up of carbon (C), aluminum (Al) and iron (Fe). Al is used as the buffer layer and Fe is used as the catalyst.

Table 1: CNT composition from EDX analysis

Element	Weigh (%)	Atomic (%)
C	89.33	97.34
Al	0.64	0.31
Fe	10.02	2.35
Total	100.00	100.00

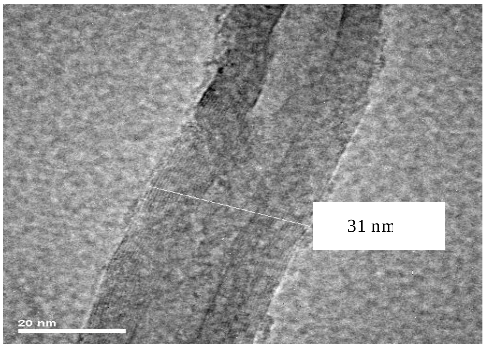

Fig. 3: TEM image of carbon nanotubes

The TEM image shown in Fig. 3 describes the multiwalled type with typical diameter of 31 nm. This proves that the CNT sample under test is a multi-wall CNT.

The phase identification of the CNT was performed by X-ray diffraction (XRD) on a Philips Pw-1730 X-ray diffractometer, using Cu Kα radiation (λ=1.54 A°).

XRD is used to measure the crystal size and interlayer spacing. Due to CNTs intrinsic nature, the main features of X-ray diffraction pattern of CNTs are close to those of graphite as shown in Fig. 4 (Berlin and Epron, 2005).

Comparison between Fig. 4 and 5 shows that a graphite-like peak (0 0 2) is present at ~28° in 2θ. Measurements of interlayer spacing (d-spacing) and crystal size (d) can be achieved from this peak (Table 2) and Scherrer equation (Eq. 1).

As mentioned above the average crystallite sizes of the MWCNT was determined by using the XRD patterns, via the well known Scherrer equation:

$$d=\frac{k\lambda}{\beta\cos\theta}=59.328\ \text{nm} \qquad (1)$$

where, λ is the x-ray wavelength, typically 1.54 Å; β is the FWHM (full width at half max) or integral width in radians; k is the shape factor dependent on crystallite shape, k = 0.9 for FWHM and 1.05 for integral breath; θ is the Bragg angle and d is the average crystal size.

Scherrer equation is driven from Bragg's law and it is limited to nano-scale particles only.

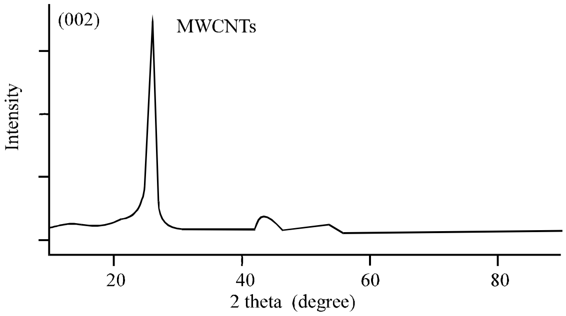

Fig. 4: A sample MWCNT XRD from (Gouadec and Colomban, 2007)

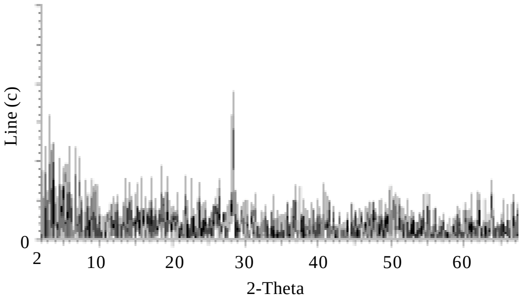

Fig. 5: Obtained MWCNT sample under test XRD result

Crystallinity can be derived from Raman spectroscopy. Having better crystallinity would result in faster movement of electron as they would not be hindered by defects such as vacancies, discontinuity, trapping centers etc. This will result in better sensitivity. A Raman spectroscopy in frequency range of 100 to 1800 cm^{-1} has been done as shown in Fig. 6. The spectra in Fig. 6 shows two main peaks, respectively named D-band and G-band. The fact that there is only one peak from 1570 to 1590 cm^{-1} proves that the sample is a MWCNT, as for the SWCNTs, there will be two peaks in the specified range. D-band arises from the nanotubes structural defect while G-band signifies the formation of well graphitized carbon nanotubes. The ratio of G-band density to D-band density (I_d/I_g) has been used to determine the crystallinity of CNT samples. From Fig. 6, I_d/I_g = 0.8, which is a good value for a MWCNT. This is evident from the well defined walls displayed in the TEM image (Fig. 3).

There is another peak happening around 270 cm^{-1} which is called Radial Breathing Mode (RBM) and it's the result of the most inner CNT wall vibration. RBM peak is not visible in MWCNTs due to interferences between inner walls (Costa *et al*., 2008; Dresselhaus *et al*., 2005).

Electrical characterization: Hall Effect measurement method was used to identify the electrical characterization

Table 2: Obtained results from XRD

Results from XRD			Constant values	
2θ	FWHM	d-spacing	k	λ
28°	0.138°	3.15715 (Å)	0.9	1.54056 (Å)

Table 3: Ecopia hall effect measurement results

Ecopia results	Values
Resistivity	0.517 x 10-2 Ω cm
Conductivity	1.934 x 102 1 Ω cm
Mobility	3.752 x 102 cm² Vs⁻¹

Table 4: Measured voltages from ecopia hall effect

Measured voltages (V)	Values	Measured voltages (V)	Values
V_{ACp}	-0.063	V_{ACn}	0.009
V_{CAp}	-0.064	V_{CAn}	0.008
V_{BDp}	-0.063	V_{BDn}	0.004
V_{DBp}	-0.069	V_{DBn}	0.003

Table 5: Hall voltage obtained from Table 4 and Eq. 2

Hall voltage (V)				
V_C	V_E	V_D	V_F	V_H
-0.067	-0.072	-0.072	-0.072	-0.283 → n-type

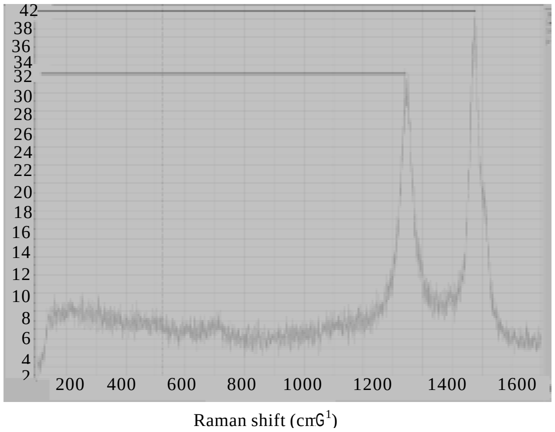

Fig. 6: Raman spectroscopy result

of the sample, using this method; conductivity, resistivity, hall voltage, carrier type, and mobility of the MWCNT sample were identified.

To do this measurement, The CNT sample is connected to an electronic plate and is placed inside a magnetic field. Ecopia software was used to monitor the measured data by applying a current charge from -1 to 1 mA, for a step size of 10. The sample thickness and magnetic flux are required as input values. The testing was done for different magnetic flux values and in all cases the resistivity and conductivity values were fixed. Here the sample thickness (D) and magnetic flux (B) values are respectively 0.559 mm and 0.2 T. The acquired results from Ecopia software are shown in Table 3 and 4.

Table 3 shows the MWCNT conductivity, resistivity and mobility values obtained from Ecopia Hall Effect measurement. From Table 3, it can be seen that the vertically aligned MWCNT sample has a good conductivity of around 1.934×10²(Ω⁻¹ cm⁻¹) which is higher than the value reported by Thaha (2008) for the non-aligned MWCNT sample. The higher conductivity will result in lower breakdown voltage.

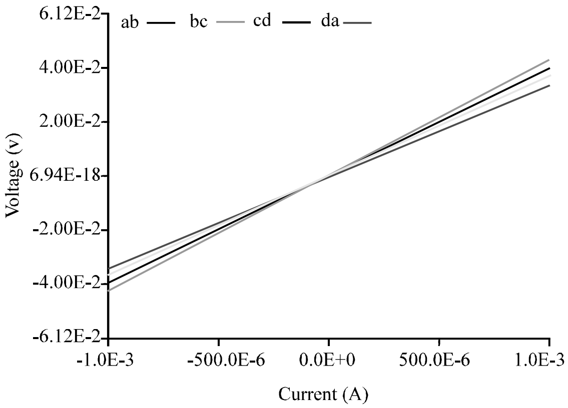

Fig. 7: Ecopia Hall Effect; voltage vs. current

Higher mobility would means faster electron transport that results in faster response time. This will make the sensor to trigger earlier warning once gas leakage is detected and so it results in safer environment.

Table 4 shows the voltage values obtained from Hall Effect device. These values are used to find the Hall voltage and carrier type.

V_{AB}, V_{BC}, V_{CD}, V_{DA}, V_{BD} and V_{AC} are voltages between each two corners of the CNT sample, respectively named; A, B, C and D. The obtained results from Table 4 and the following equations are used to calculate the Hall voltage (V_H).

Hall offset voltage:

$$V_H = V_C + V_D + V_E + V_F \qquad (2)$$

Where;

$$V_C = V_{BDp} - V_{BDn} \quad V_D = V_{DBp} - V_{DBn}$$
$$V_E = V_{ACp} - V_{ACn} \quad V_F = V_{CAp} - V_{CAn}$$

The polarity of V_H from Eq. 2 defines the sample type, for positive sum the sample type is p-type and for negative sum it is an n-type. Calculations are shown in Table 5, the result shows that the current sample under test is an n-type.

Figure 7 and 8 show the CNT voltage vs. current and resistance vs. current plots between each two points of the CNT sample, respectively. The obtained resistance is

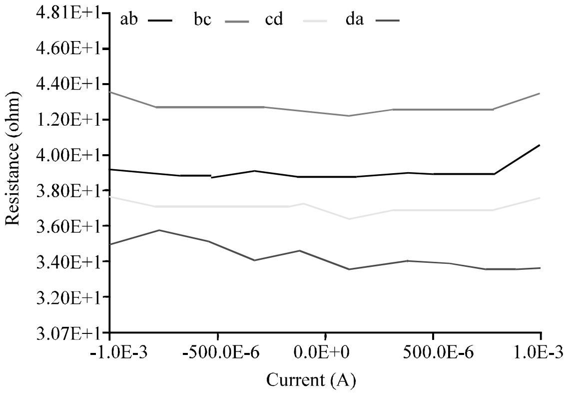

Fig. 8: Ecopia Hall Effect; resistance vs. current

10 times smaller than the value achieved form Thaha (2008) for non-aligned MWCNT, which results in better conductivity.

CONCLUSION

In this study, the vertically aligned carbon nanotubes array was used as gas sensing element. From FESEM spectroscopy, the CNT array is found to be vertically aligned.

From Hall Effect measurement, the resistivity and conductivity of the sample were measured. The sample was found to be more conductive compared to non-aligned MWCNT sample.

A Raman microscopy has been done and the result proved that the sample under test is a MWCNT with better crystallinity and so better sensitivity compared with non-aligned sample.

All these, higher conductivity, mobility and crystallinity would indicate better sensing properties as in lower break down voltage, faster response time and better sensitivity. All these results show the effect of alignment on the performance of the sensor. The utilization of highly aligned CNTs will result in higher selectivity and sensitivity. It will also result in the lowering of the breakdown voltage due to high linear electric field near nanotube tips and shorter electric path.

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