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Piezoresistive Effect of Aligned Multiwalled Carbon Nanotubes Array

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Abstract: There is a growing interest to exploit the mechanical properties of carbon nanotubes (CNTs) for electromechanical sensor as they exhibit supercompressibility, resilience and large elastic modulus. The paper presents the study of piezoresistive effect in aligned multi-walled carbon nanotube (CNT) array grown by chemical vapor deposition. When the array is compressed, individual carbon nanotubes start to buckle, which in turn decreases the array's electrical resistance. This behavior was found to be almost fully recoverable for the loading of up to 500 g with an increment of 50 g at an interval of 10 and 50 sec. The recorded drop in resistance during the application of the load is attributed to an increasing number of conduction channels in the nanotubes array. The change in the resistance was also found to increase linearly when 100 and 500 g load was applied at a temperature of 20 to 180°C. These results in higher values of piezoresistive effect, making MWCNTs array a very effective sensing element for pressure and strain sensor operating at elevated temperature.

Key words: Carbon nanotubes, catalyst, chemical vapor deposition, sandwich configuration, buffer layer

INTRODUCTION

Currently a tremendous amount of research activities to exploit the remarkable properties of carbon nanotubes (CNTs) has been carried out in order to realize their practical applications. Driven by high compressive strength (Yu *et al.*, 2000) and large elastic modulus of CNTs (Iijima *et al.*, 1996; Qian *et al.*, 2002; Sazonova *et al.*, 2004), electromechanical properties have started to be investigated for possible application as electromechanical sensor. Electromechanical properties of CNTs were found to be better than the traditional materials because of their high elastic modulus coupled with their unique electrical properties that can be metallic, semiconducting and semi-metallic depending on the orientation of the atomic lattice with respect to the axis of the tube and the diameter. Although extensive studies have been conducted on electrical and mechanical properties of CNT reinforced polymer (Chopra *et al.*, 1995; Despres *et al.*, 1995; Treacy *et al.*, 1996), only few have actually been reported on the CNT behavior in its original state (Pushparaj *et al.*, 2007). Tombler *et al.* (2000a) had observed the drop in the conductance of metallic carbon nanotubes by two-orders of magnitude when strained by the tip of atomic force microscope. The resistance of single-walled carbon nanotubes was found by Tombler *et al.* (2000b) to vary significantly under bending and trenching.

Unlike Cao *et al.* (2007) who reported on temperature dependent piezoresistive of MWCNT film with random alignment, the study here focused on the piezoresistive effect of well-aligned MWCNT array in its original form when the mechanical load is being applied. Temperature dependent piezoresistive effect of pristine nanotube array was also investigated. MWCNTs array was grown by catalytic CVD method (Lai *et al.*, 2008). The two equal size wafer substrates with.

MWCNTs film is placed on top of each other in a sandwich configuration in order to obtain the double layer. The sandwich configuration of CNTs offers better compressibility with its thicker height and easy handling during integration of contacts for the testing.

The piezoresistive effect describes the changing electrical resistance of a material due to applied mechanical stress. The phenomenon was first discovered in 1856 by Lord Kelvin and later in 1954, large piezoresistive effect was found to be exhibited by silicon and germanium (Smith, 1954). The sensitivity of piezoresistive devices is characterized by the gauge factor:

$$K = \frac{dR}{R\varepsilon} \tag{1}$$

where, dR is the change in resistance due to deformation, R is the undeformed resistance and ϵ is the strain. In the

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Table 1: Gauge factors for typical materials

Materials	Gauge factors	Materials	Gauge factor materials
Platinum	4.0	Small gap semiconducting CNT	600-1000
Aluminum	2.5	CNT (Semiconducting)1	50
Copper	2.2	Silicon (p-doped)	126
Gold	2.1	CNT (metallic)	40-60

piezoresistive theory, the gauge factor, K can be further defined as (Middelhoek and Audet, 1989):

$$K = 1 + 2\nu + \frac{d\rho}{\rho_0 d\varepsilon} \qquad (2)$$

where ν is Poisson's ratio of the films, ρ and ρ_0 are resistivities for strain ϵ and 0, respectively. In Eq. 2, the gauge factor, K can be divided into two terms which is expressed as $(1 + 2\nu)$ due to geometrical deformation and $(d\rho/\rho_0 d\varepsilon)$ due to the change in the electrical resistivity of the material. If the resistance change resulting from strain is due to only geometrical changes, K derived from the first term would be a small value. Thus the geometrical changes cannot account for the large gauge factor observed in some materials.

Gauge factors for a number of materials namely metal, semiconductors, CNTs have been reported as listed in (Table 1) (Cao *et al*., 2003; Kane *et al*., 1998). Although the piezoresistive effect in metals due to the stress, dependent change of geometry is very small compared to the values of other materials, they have been successfully used in a wide range of applications (Window, 1992). The piezoresistive effect of semiconductor materials such as germanium, polycrystalline silicon, amorphous silicon, silicon carbide, and single crystal silicon was found to be several orders of magnitudes larger than the geometrical piezoresistive effect in metals. This is because the resistance of silicon changes not only due to the stress dependent change of geometry, but also due to the stress dependent resistivity of the material, resulting in gauge factors of the orders of magnitudes larger than those observed in metals (Smith, 1954). Cao *et al*. (2003) had verified the superiority of mechanical properties of CNTs amongst the materials with the finding of the highest gauge factor for narrow-gap semiconducting type CNT.

MATERIALS AND METHODS

Two equal size substrates of Si wafers were deposited with 300 nm SiO_2, followed by Al_2O_3 buffer layer and final coating of Fe catalyst. These coated substrates were then annealed at 400°C for 2 h before being subjected to NH_3 etching at 850°C for 10 min and cooling to room temperature. MWCNTs array was grown using CVD system maintained at 700°C with ethylene flowed in at 700 Sccm for 10 min (Lai *et al*., 2008). Then hydrogen was purged in at 500 Sccm until the system cooled down to 300°C and to room temperature with the flow of argon. The as-produced nanotubes array was then analyzed by scanning (SEM) and transmission electron microscopy (TEM).

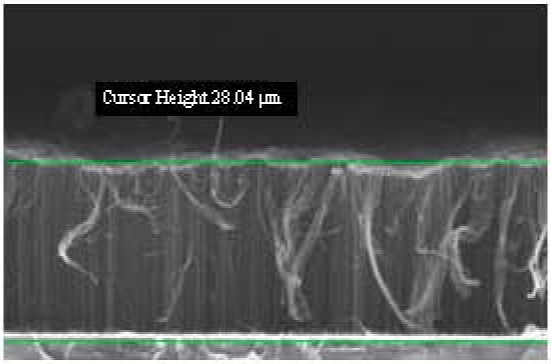

Fig. 1: SEM image of MWCNTS film on the substrate

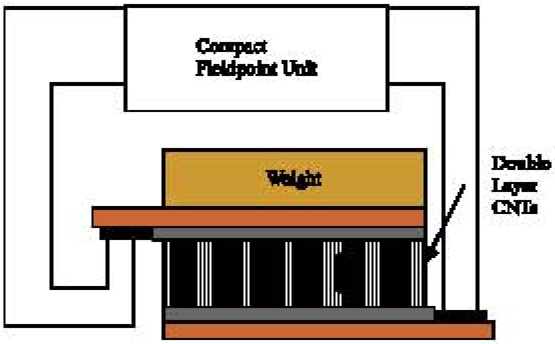

Fig. 2: Schematic diagram of the measurement unit

The product as shown in Fig. 1 is in the form of well- aligned MWCNTs film with typical height of 28 µm. As depicted in Fig. 2, the two equal size substrates are placed on top of each other with MWCNTs array in between forming double layer of typical height of 59 µm. Contacts were made on the conductive base at the sides of CNTs array as shown in the schematic diagram of the test unit in Fig. 2. All connections were made to the Compact Fieldpoint (National Instrument) for the purpose of converting all input/output signals, namely the voltage and current, from the test unit to the relevant computerized data and display using LabView software.

Mechanical stress in the form of loading was applied parallel to the axis of CNTs. Weight added was in an increment of 50 g to a maximum of 500 g at different time interval (10, 50 and 100 sec) between additions of weights. Electrical resistance was then measured against time for the loading time interval of 10, 50 and 100 sec.

RESULTS AND DISCUSSION

Figure 3 shows the SEM image of well-aligned CNTs film. The part that is not covered by nanotubes forest is obtained by omitting the deposition of catalyst film prior to the growth process. This part is designated for the electrical contact required for the measurement of the electrical behavior. TEM analysis shown in Fig. 4 described the multiwalled type with diameter in the range of 30 to 50 nm. In the above measurement, the load was applied to nanotubes array by continuously added with 50 g weight at a time until 500 g and then released with the removal of 50 g at a time until completely free of the load. It is observed from Fig. 5a and b that almost full recovery of the initial resistance value is obtained for the loading 10 sec (99%) and 50 sec (93%). However for the longer loading interval of 100 sec (Fig. 5c), no recovery was recorded indicating the occurrence of creep phenomenon (Finnie and Heller, 1959).

The decrease in resistance is attributed to the interval of bending of CNTs that lead to overlapping of electron states in adjacent nanotube walls resulting in an increase in the accessible number of conduction channels (Semet *et al*., 2005) . As shown in Fig. 6, when the change of resistance is plotted against weight applied, the curve describes the initial drastic increase in

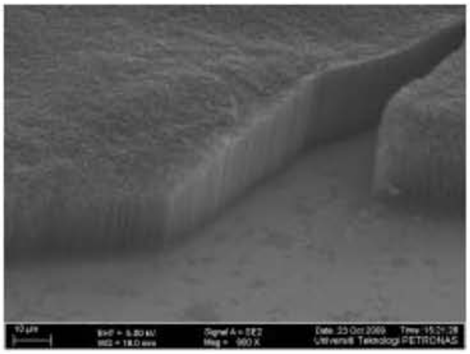

Fig. 3: SEM image of large area of MWCNTS film with the uncovered part of the substrate available for the electrical contact

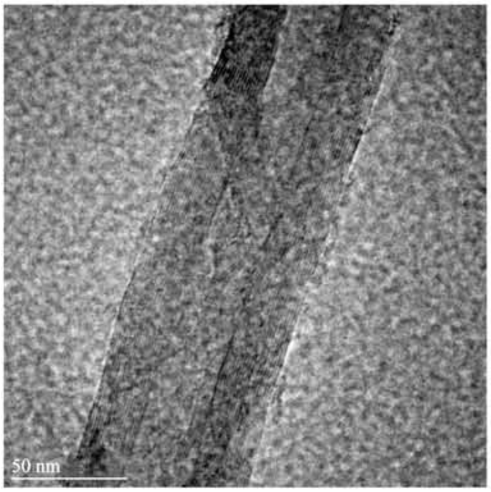

Fig. 4: TEM image of carbon nanotube

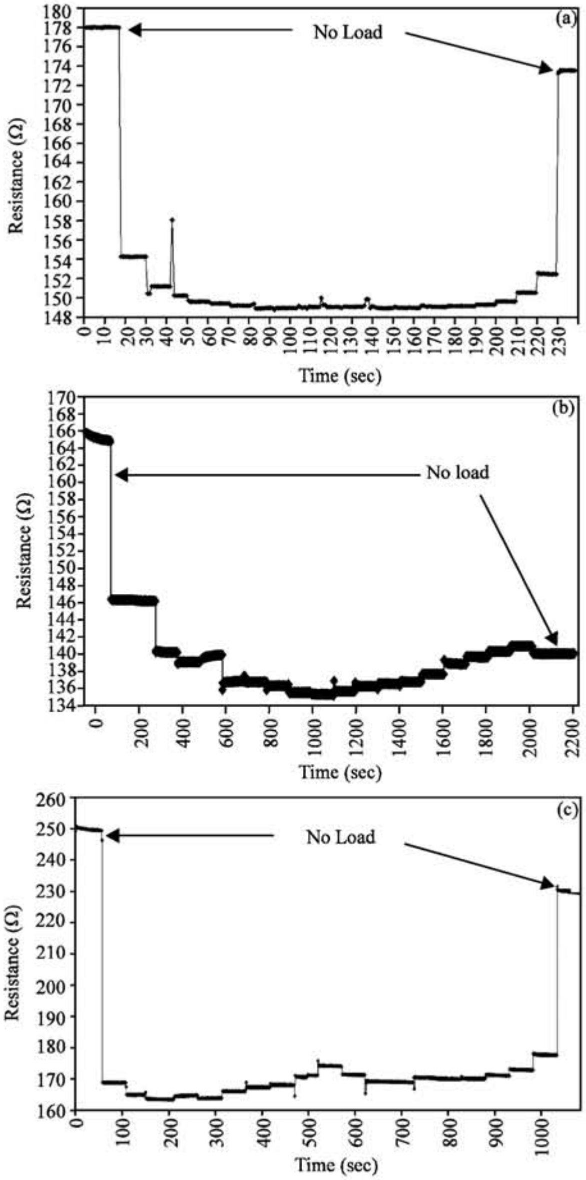

Fig. 5: A plot of resistance against time on applying the load with an increment of 50 g for the loading time interval of (a) 10, (b) 20 and (c) 100 sec

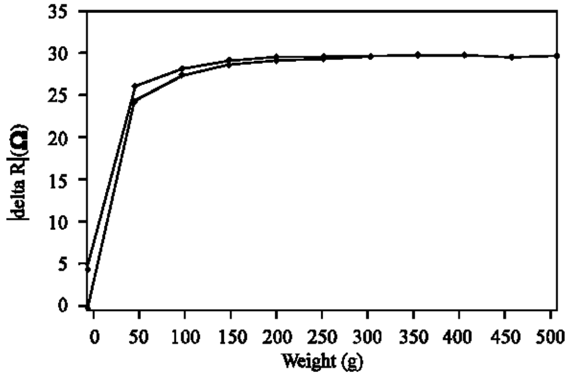

Fig. 6: A change in resistance, |ΔR| (Ω) as a function of the weight applied, w (g)

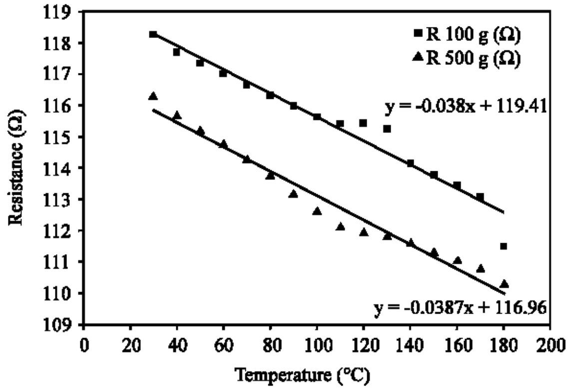

Fig. 7: Plot of resistance (ohms) against temperature (°C) for 100 g (■) and 500 g (▲) load

resistance followed by gradual decrease in the change of resistance and finally tapers off when it reaches 350 g. Hysteresis effect (Lemaitre and Chaboche, 1990) is observed where there is a slight difference between the values with increasing weights and decreasing weights with the latter recording a change of resistance of 5 ohm upon total removal of the load.

In order to understand the effect of temperature on the resistance as the load is been applied to the nanotubes array, measurement were also carried out by varying the temperature from room temperature, 20 to 180°C. When the weights of 100 g and 500 g were applied to nanotubes array, linear decrease in resistance values were registered as described in Fig. 7. Values of the gauge factor could not be calculated as the strain measurement was not carried out experimentally here. However, from Eq. 1 an increase in the change of resistance, dR would result in an increase in the gauge factor. This finding of an increased dR with temperature is agreeable with Cao *et al.* (2007) who discovered a rapid increase in the gauge factor with an increase in temperature of up to 50°C.

CONCLUSION

The resistance was found to decrease on the application of the load and upon removal of the applied load; the resistance value almost retains its original value with 99% for the 10 sec loading interval and 93% for the 50 sec loading interval The study on the temperature dependent piezoresistive effect has shown that MWCNTs array exhibits a significant increase in the change of resistance with increasing temperature of 20 to 180°C. This implies that higher gauge factor, K can be achieved by increasing the temperature. Physically, applying load causes the array structure to become denser allowing more contact between nanotubes and resulting in higher conduction. On removing the load from the CNT array, the electrical resistance almost regained its original no-load value. The high elasticity of the covalent carbon-carbon bonds is responsible for the return to its original state even from a strong deformation. This property combined with the remarkable electrical response to the mechanical load makes CNT array a suitable and effective sensing element for pressure or strain sensor operating at elevated temperature.

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