ARTICLE

HIGH PIEZORESISTIVE BEHAVIOR OF VERTICALLY ALIGNED MULTI-WALL CARBON NANOTUBES ARRAY

Vahid Mansouri[1], Amir Yadegari [2], A Rashidi [4], Mohammadmehdi Choolaei [4], Meisam Omidi [2, 3*]

[1]Proteomics Research Center, Faculty of Paramedical Sciences, Shahid Beheshti University of Medical sciences, Tehran, IRAN

[2] Research Centre for Medical Nano-Technology and Tissue Engineering, School of Advanced Technologies in Medicine, Shahid Beheshti University of Medical sciences, Tehran, IRAN

[3]Department of Tissue Engineering and Regenerative Medicine, School of Advanced Technologies in Medicine, Shahid Beheshti University of Medical sciences, Tehran, IRAN

[4]Research Institute of Petroleum Industry (RIPI), Tehran, IRAN

ISSN 0976-3104

ABSTRACT

Due to their unique electrical, mechanical, and electromechanical properties, vertically aligned carbon nanotube (VACNT) films are promising to be used as piezoresistive based sensors. When VACNT is subjected to mechanical deformations, its resistance changes dramatically. This effect can be utilized for strain sensing, pressure sensing, and also for nanoelectromechanical transducers in micro electromechanical systems (MEMS). In this work, at first a simple method was employed to fabricate VACNT films within the cylindrical pores anodic aluminum oxide (AAO) substrate. Then, electronic and mechanical properties of VACNTs were obtained after removing AAO substrate. Finally, by using VACNT films, which were attached to a paper substrate, a mechanically flexible load sensor was fabricated. Experimental results show that using VACNT film instead of random orientation carbon nanotube film increases gauge factor of the sensor, which is an important designing factor.

KEY WORDS
Unique electrical, mechanical, (AAO) substrate, vertically aligned carbon nanotube (VACNT)

Received: 22 Aug 2016
Accepted: 17 Sept 2016
Published: 5 Oct 2016

***Corresponding Author**
Email:
m_omidi@sbmu.ac.ir

INTRODUCTION

Unique structural of Carbon nanotubes (CNTs) such as electromechanical features, thermal properties, and high aspect ratio, introduce them as an ideal sensing component for piezoresistive sensors [1]. The piezoresistive effect in CNTs has been investigated for the first time by Tombler et al. [2]. For instance, the gauge factor of CNTs was reported to be about1000, which is five times larger than that of single crystal silicon. Other measurement presented by Cao et al. [3] illustrated a gauge factor up to 3000 for individual single wall carbon nanotubes (SWCNTs). In another research,Obitayo and Liu [4], have presented some important features of CNTs for strain sensing. Dharap et al. [5] have used pure SWCNT films (bulky paper) as a sensing component in strain sensors. Further studies were presented by Li et al. [6] using thin film of nanotubes as strain sensor. The film was made of randomly orientated bundles of SWCNTs and was attached to a rubber strip using epoxy. Another concept with multi walled carbon nanotubes (MWCNTs) film was reported recently by Li et al. [7] and Song et al. [8].

For practical application, Pham et al. [9] have fabricated poly (methyl methacrylate) (PMMA)/MWCNT composite films based sensor. Also, a new type of polyisoprene/MWCNT composite strain sensor was reported by Knite et al. [10]. Kang et al. [11] and Loh et al. [12] have cited the use of CNT/polymer composites as strain sensors for structural health monitoring. Piezoresistive behavior of CNTs has also been applied for pressure sensors [13, 14] and force sensors [15]. Due to CNTs random orientation, the gauge factor was found to be rather small for CNT films [16-17] that may hinder the potential application of CNTs. To overcome the above mentioned limitation of CNTs, using vertically aligned carbon nanotube has been recently investigated [18-22].

This paper presents the concept and demonstration of nano electromechanical sensors based on vertically aligned carbon nanotubes (VACNTs). At first, the VACNT films were synthesized on the porous anodic aluminum oxide (AAO) substrate by using chemical vapor deposition (CVD). Here, the AAO is used as a substrate for growing VACNTs. The proposed method possesses numerous advantages such as fast alignment, facile array design, mass production, high level of structural diversity, and complexity. The electronic and mechanical properties of VACNTs were then obtained after removing AAO. Finally, by using VACNT films, which were attached to a paper substrate, a mechanically flexible load sensor was fabricated. Electromechanical measurements reveal that the VACNT films can be utilized as an exceptional piezoresistive electromechanical transducer with higher gauge factor values in comparison with the state-of-the-art strain gauges.

MATERIALS AND METHOD

The process of preparing AAO substrate contains two steps, as follow: in the first step, bath ultrasonic was used for aluminum foil cleaning. After that, it was electrochemically brushed by ethanol and perchloric acid (HClO4) solution under constant voltage of 20 V for 2 min to achieve a mirror-like surface. Anodization

IIOAB JOURNAL
ISSN: 0976-3104

process was carried out in an electrochemical cell at the temperature of 10 ◦C. The first anodization process was carried out using 0.2 M oxalic acid under 40 V for 2 h. The formed porous oxide film was chemically removed using a solution consisting of the following weight percent: 6% phosphoric acid (H3PO4) and 1.8% chromic acid (H2CrO4). This process was carried out at 65 ◦C for 2 h. Second anodization was carried out under the same conditions of the first anodization for 58 h. Then, in order to achieve through-hole membrane, one side of AAO was covered by preserving polymer.. This sample was submerged in 5% (wt) phosphoric acid (H_3PO_4) for 3 h, and the temperature was kept at 50 ◦C. Afterwards, the sample was placed in saturated mercuric chloride ($HgCl_2$) solution to separate aluminum, the preserving polymer was also mechanically separated. Then, the barrier layer was removed using 5% (wt) of phosphoric acid (H_3PO_4) at the temperature of 30 ◦C for 60 min. Finally, anodic alumina substrate was preheated by being pressed between two α-alumina disks at 800 ◦C for 1 h to enhance its stability. This process is necessary to avoid fracturing and curling of substrate which usually occurs during phase transition of the amorphous alumina. The FESEM surface images of AAO synthesized are shown in [Fig. 1a].

Preparation of CNTs within the AAO substrate was carried out using chemical vapor deposition (CVD) method in a tubular electrical furnace (DI=50 and L=1100 mm). The controlled flow of C2H2 and Ar was injected into the reactor as the carbon precursor and carrier gas, respectively. The AAO substrate was vertically placed in the furnace, and temperature increased with a rate of 5 ◦C/min from room temperature to 650 ◦C under Ar flow (200 ml/min). The ratio of C_2H_2/Ar was adjusted to be about 0.01 when the reactor temperature reached to 650 ◦C. Afterwards, the acetylene (C_2H_2) flow was removed and the reactor was cooled to room temperature under the atmosphere of Ar. CNTs membranes were also put in 200 ml/min flow of O2 at 400 ◦C for 1 h under smooth oxidative treatment. Finally, all samples were washed by ethanol (C_2H_6O) and dried in 60 ◦C for 4 h under vacuum condition. [Fig. 1b] shows the image of VACNTs after removing AAO and the TEM images of fabricated CNTs are presented in [Fig. 1c].

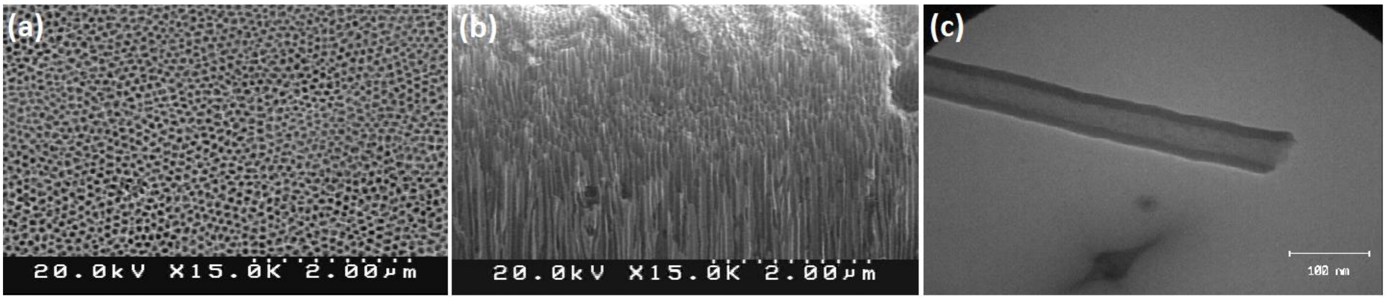

Fig. 1(a): FESEM image of AAO substrate prepared by anodization process. (b) FESEM image of VACNTs after removing AAO (c) TEM image of VACNTs

In order to prepare the VACNTs/paper-based load sensor, an A4 paper with a thickness of 340 μm was chosen as the substrate, and it was patterned to the required dimensions (80 mm × 8 mm) using a laser cut with a precision of 0.12 mm. In the next step, the electrical contact pads were printed using a silver ink. Then VACNTs film (5×5 mm) was attached to the paper substrate. In order to certify the connections between the printed contact pads and sensing components (VACNTs film) a small drop of silver ink was placed on the connections using a painting brush. Moreover, in order to protect the connections a nylon film was placed on the top and bottom of the sensor using a paste. At the end, by connecting the contact pads to the multimeter (Keithley 2400 source meter), it was possible to read the resistance change of the system. A simple illustration of the VACNTs/paper-based load sensor can be observed in [Fig. 2].

RESULTS AND DISCUSSION

All the measured voltage-current (V-I) characteristics of VACNTs film showed a linear ohmic V-I behavior [Fig.3]. This matter indicates the correlation between the piezoresistivity of VACNTs film and the deflection caused by the loaded force. The results determined a resistance of 2.8 kΩ and 115 kΩ corresponding to parallel and perpendicular CNT directions.

In order to perform the relation between the applied compressive strain on the VACNTs film (input) and resistance change (output) we have calibrated the VACNTs/paper-based sensor by using a multimeter. [Fig. 4] shows the resistance of the VACNTs at each measurement step. When the paper-based sensor is unloaded, VACNTs' resistance has returned to its initial value. This confirms that the original VACNTs –silver contact was a firm contact, i.e. slipping between VACNTs –silver contact did not occur during the experiments.

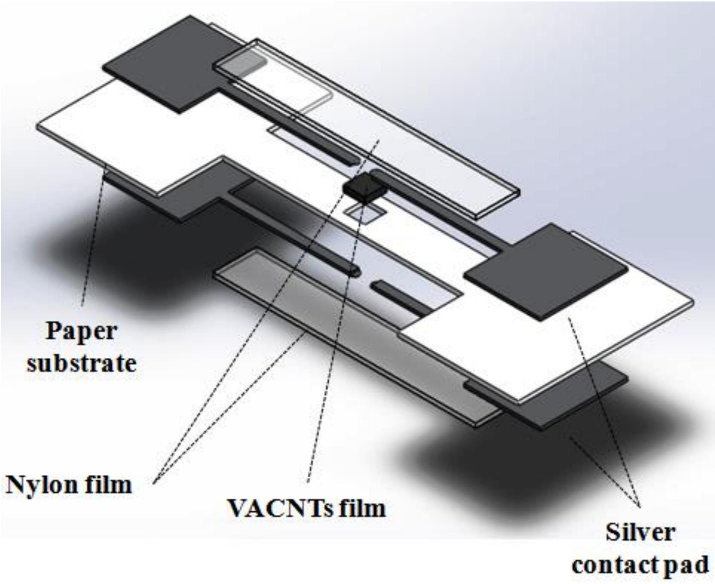

Fig. 2: Schematic view of a VACNTs/paper-based load sensor

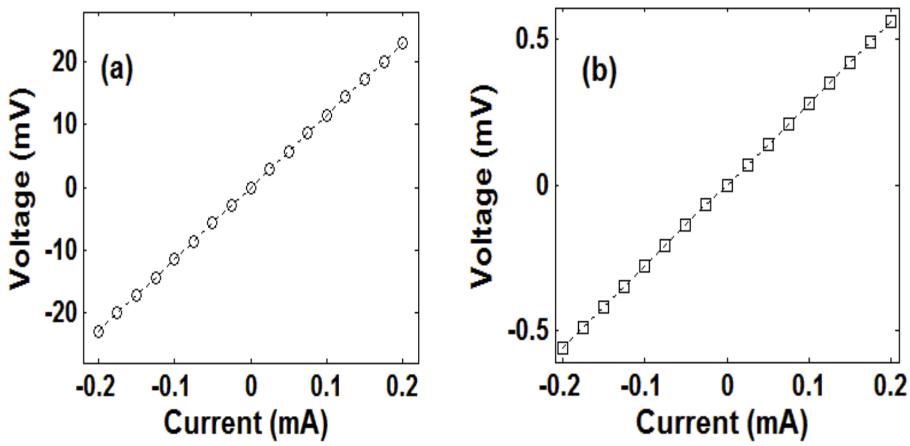

Fig. 3: Linear current–voltage curves for VACNTs film (a) perpendicular and (b) parallel

Since the VACNTs are strongly attached to the surface of the sample, and the dimension of testing element is ignorable compared to the paper substrate, it is reasonable to assume that the maximum strain in the middle of the beam is completely transferred to the VACNTs. The strain in the sample can be written as below

(1) $$\varepsilon = \frac{3FL}{4EWH^2}$$

where the young's modulus is shown by E, the applied force is presented by F, and the length, width, and thickness of the paper beam are shown by L, W, and H, respectively.

In order to compare the results from VACNTs/paper-based sensor and literature, the gauge factor G can be calculated as:

(2) $$G = \frac{\Delta R / R_0}{\varepsilon}$$

Where ε and ΔR are the strain and relative change of resistance, respectively.

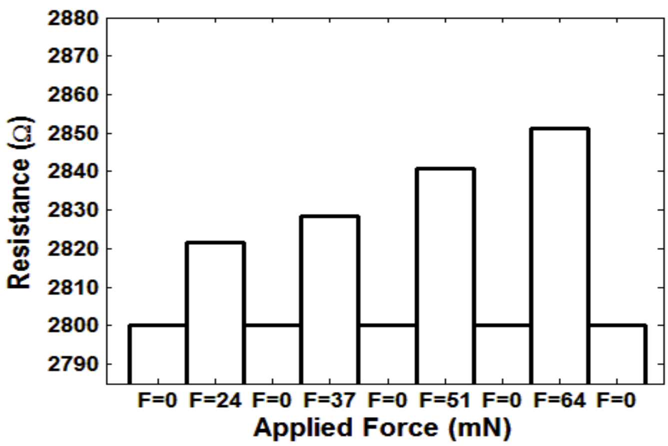

Fig. 4: The electrical resistivity variation of longitudinal VACNTs against applied force (Unload condition indicated when F=0).

………..

[Fig. 5] shows the relation between the relative resistances (ΔR/R) versus applied strain of VACNTs element. The longitudinal (GL) and transverse (GT) gauge factors, measured when the VACNTs are respectively aligned with longitudinal stress direction, are GL= 9.07 and GT = 0.76. The results presented a linear resistance change with the applied forces. The sensitivity of the VACNT film was found out to be 1.9 mVmN-1. Moreover, by studying [Fig. 5] the range of linearity and force resolution were found to be 110 mN and 50 μN, respectively.

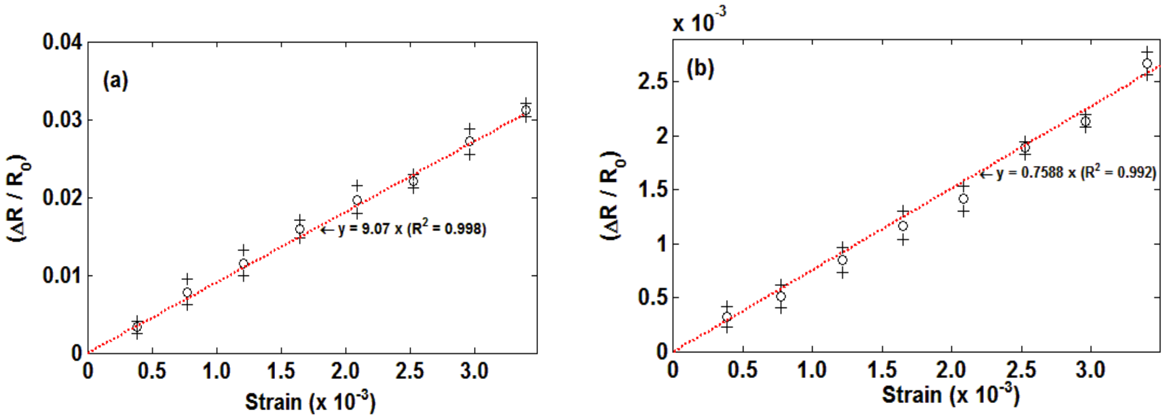

Fig. 5: Relative change of resistance against the applied mechanical strain of VACNTs (a) longitudinaly and (b) transversely aligned directions.

………

As it can be observed in [Table 1], the measured gauge factor values of VACNTs are about 3 times higher than the gauge factor of CNTs film [7 and 8] and bundle [17], which have been previously reported in literature. The higher gauge factor of VACNTs indicates higher sensitivity of this sensor, in comparison with other reports.

[Table 1]: Measured gauge factors value of CNTs.

Work	gauge factor
This work (VACNTs)	9.07 (longitudinal)
	0.76 (transverse)
X Li et al. [7] (MWCNTs film)	2–3.76
Song et al. [8] (MWCNTs film)	0.01–1.25
Sickert et al. [17] (SWCNTs bundle)	2

On the other hand, the presented gauge factors are far away from that individual CNT reported by Tombler et al. [2] and Cao et al. [3].

In this work, the calculated gauge factor is the result of the integration of CNTs instead of single CNTs, leading to a lower gauge factor in comparison with published works with much higher gauge factor. Due to the imperfect alignment of the nanotubes in the forest, nanotubes might form small bundles. This imperfection provided the essential lateral interconnection for mechanical cohesiveness, but deteriorated the principal orientation of the sensing element.

CONCLUSION

In this paper, an attempt has been made to use the piezoresistive effect of vertically aligned carbon nanotubes in the sensing applications. We have developed a paper-based sensor based on piezoresistive property of VACNTs for measuring the magnitude of applied load. We have prepared anodized aluminum oxide substrate, and VACNTs film through the aforementioned process. The results showed that using VACNTs film increased the gauge factor (GL= 9.07 and GT = 0.76) and subsequently improved the sensitivity of the system. VACNTs exhibited the following characteristics: range of linearity of 110 mN, force resolution of 50 µN, and the sensitivity of 1.9mV.mN-1.

CONFLICT OF INTEREST
There is no conflict of interest.

ACKNOWLEDGEMENTS
None

FINANCIAL DISCLOSURE
None

REFERENCES

[1] Maiti A, Svizhenko A, Anantram MP. [2002]. Electronic transport through carbon nanotubes: Effects of structural deformation and tube chirality. Physical review letters, 88(12), 126805.

[2] Tombler TW, Zhou C, Alexseyev L, et al. [2000]. Reversible electromechanical characteristics of carbon nanotubes under local-probe manipulation. Nature, 405 (6788), 769-772.

[3] Cao J, Wang Q, Dai H. [2003] Electromechanical properties of metallic, quasimetallic, and semiconducting carbon nanotubes under stretching. Physical review letters, 90(15), 157601.

[4] Obitayo W, Liu T. [2012] A review: carbon nanotube-based piezoresistive strain sensors. Journal of Sensors, 2012.

[5] Dharap P, Li Z, Nagarajaiah S et al. [2004] Nanotube film based on single-wall carbon nanotubes for strain sensing. Nanotechnology,15(3), 379.

[6] Li Z, Dharap P, Nagarajaiah S, et al. [2004] Carbon nanotube film sensors. Advanced materials, 16(7), 640-643.

[7] Li X, Levy C, Elaadil L. [2008] Multiwalled carbon nanotube film for strain sensing. Nanotechnology, 19(4), 045501.

[8] Song X, Liu S, Gan Z et al. [2009] Controllable fabrication of carbon nanotube-polymer hybrid thin film for strain sensing.Microelectronic Engineering, 86(11), 2330-2333.

[9] Pham GT, Park Y B, Wang B. [2005] Development of Carbon-Nanotube-Based Nanocomposite Strain Sensor. In ASME 2005 International Mechanical Engineering Congress and Exposition (pp. 987-993). American Society of Mechanical Engineers.

[10] Knite M, Klemenok I, Shakale G. et al. [2007] Polyisoprene–carbon nano-composites for application in multifunctional sensors. Journal of alloys and compounds, 434, 850-853.

[11] Kang I, Schulz MJ, Kim JH et al. [2006] A carbon nanotube strain sensor for structural health monitoring. Smart materials and structures, 15(3), 737.

[12] Loh KJ, Kim J, Lynch J. et al. [2007] Multifunctional layer-by-layer carbon nanotube–polyelectrolyte thin films for strain and corrosion sensing. Smart Materials and Structures, 16(2), 429.

[13] Fung CK, Zhang MQ, Chan R H et al. [2005] A PMMA-based micro pressure sensor chip using carbon nanotubes as sensing elements. In 18th IEEE International Conference on Micro Electro Mechanical Systems, 2005. MEMS 2005. (pp. 251-254). IEEE.

[14] [14] Stampfer C, Helbling T, Obergfell D. et al. [2006] Fabrication of single-walled carbon-nanotube-based pressure sensors. Nano Letters, 6(2), 233-237.

[15] Stampfer C, Jungen A, Hierold C. [2006] Fabrication of discrete nanoscaled force sensors based on single-walled carbon nanotubes. IEEE Sensors Journal, 6(3), 613-617.

[16] Facca S, Lahiri D, Fioretti F. et al. [2011] In vivo osseointegration of nano-designed composite coatings on titanium implants. ACS nano, 5(6), 4790-4799.

[17] Sickert D, Taeger S, Kühne I. et al. [2006] Strain sensing with carbon nanotube devices. physica status solidi (b), 243(13), 3542-3545.

[18] Baniasadi L, Omidi M, Amoabediny G. et al. [2014] An inhibitory enzyme electrode for hydrogen sulfide detection. Enzyme and microbial technology,63, 7-12.

[19] Omidi M, Malakoutian MA, Choolaei M. et al. [2013] A Label-Free Detection of Biomolecules Using Micromechanical Biosensors. Chinese Physics Letters, 30(6), 068701.

[20] Omidi M, Alaie S, Rousta A. [2012] Analysis of the vibrational behavior of the composite cylinders reinforced with non-uniform distributed carbon nanotubes using micro-mechanical approach. Meccanica, 47(4), 817-833.

[21] Rashidi A, Omidi M, Choolaei M. et al. [2013] Electromechanical properties of vertically aligned carbon nanotube. In Advanced Materials Research 705; 332-336.

[22] Omidi M, Haghiralsadat F, Oroojalian F. et al. [2013] Fabrication of paper-based load sensor by using the multi-walled carbon nanotubes ink. In Networking, Sensing and Control (ICNSC), 2013 10th IEEE International Conference, 221-225.