Digest Journal of Nanomaterials and Biostructures Vol. 9, No. 2, April – June 2014, p. 511 - 517

CRYOGENIC SENSOR WITH CARBON NANOTUBES

E. I. IONETE[a] S. M. IORDACHE[b], A.-M. IORDACHE[b], R. E. IONETE[a], A. SALCEANU[c],C. NICHITA[b], B. DOBRICA[b], I. STAMATIN[b*]
[a]*National R&D Institute for Cryogenics and Isotopic Technologies – ICIT Rm.Valcea,4 Uzinei Str.RM Valcea, 240050, Valcea Romania*
[b]*University of Bucharest. Faculty of Physics,3Nano-SAE Research Center, P.O. Box MG-38, 077125, Magurele, Romania*
[c]*Technical University "Gh.Asachi" Faculty of Electrical Engineering, Bd. DimitrieMangeron 53, Iassy, Romania*

Two resistive structures designed with carbon nanotubes aligned by dielectrophoretic method from dropcasted solutions, THF-Nafion, are proposed as microsensors for temperature measurements in the cryogenic field up to 77K. The activation energy, stability against ageing, and perspective to design microsensors for cryogenic applications are taking in account.

(Received February 24, 2014; Accepted April 9, 2014)

Keywords: Single wall carbon nanotubes, Cryogenic microsensor, electrophoretic alignment

1. Introduction

The variation of the resistance of electrical conductors for low and ultra-low temperature measurements remain common practices in designing of temperature sensors. The international temperature scale, ITS-90, defines five overlapping ranges. The referential for the third range (13.8033–273.16 K) use platinum resistance thermometers calibrated at the triple points of various materials [1, 2]. Other materials such as Cu, oxides, carbon or carbon-ceramic composites exploit the same principle with aim to increase sensibility, reliability and miniaturization for low temperature thermometer. Miniaturization of sensors is a challenging issue for scientists and developers of the electronic structures especially when the process need accurate measurements in specific locations, fast response, high sensitivity and low power consumption respective, low heat dissipation rates. Looking for new advanced materials to design sensors for low temperature measurements one of the most appropriate could be carbon nanotubes to replace carbon and carbon-ceramic composites, which require time consuming in ageing and the structure stabilization. The discovery of carbon nanotubes (CNTs) [3] has generated keen interest among researchers to develop sensors based CNT- [4-6] and nanoelectronic devices [7]. With superior electrical, thermal and mechanical properties [8-10] the carbon nanotubes have suggested that small-scale sensors would lead to better performance than other devices of similar size, targeting ultrasensitive nanosensors. The electronic properties in CNTs are dependent of geometrical factors (diameter and chirality) therefore they have ability to be either conducting or to have semiconductor behavior [11]. The extremely small size of the CNTs can provide accurate measurements at nanoscale with ability to be inert at perturbing factors near to the measurement point, extremely important in the cryogenics field or in the thermal flow system. In addition, the small size requires very low power consumption, in the range micro/nano-watt. Unfortunately, selection and grading CNTs in semiconductors or metallic conductors remains a challenge for synthesis. Usually high grade CNTs are supplied in bulk of bundles of metallic and semiconductors with unknown concentration.

---

[*] Corresponding author: istarom@3nanosae.org

To design a microsensor for temperature measurements in the third range with CNTs the most appropriate technique is the electrophoretic alignment. This contribution reports the temperature dependence of CNT resistance, from 77K to 300 K, activation energy. Bundles of CNTs are electrophoretic aligned between two Ag- electrodes from drop casted solution with Nafion-protective coating and compared with a standard carbon-ceramic sensor. High sensitivity in the range 200K-room temperature opens a new perspective to be used in tags or labels and integration in electronic on plastic devices.

2. Materials and methods

Materials. SWCNT, bundle of tubes with diameter 1.2-1.5 nm, length 2-5 μm, purchased from Sigma Aldrich. Carbon content 50-70%. The materials are cleaned by oxidation of the amorphous compounds in nitric-sulfuric acid, aqua regia, washed and dried. Finally, the residues are removed by thermal oxidation at 500^0C; THF (tetrahydrofuran), analytical grade, 99.9%; Nafion solution (concentration ~5% in a mixture of aliphatic alcohols and water (Golden Energy Fuel Cell Co., Ltd); Sensor support - ceramic substrate (10 x 30 mm) with two printed silver electrode (1 x 15 mm electrode length, 1.5 mm distance between electrodes).

Reference temperature sensor: type TVO-207, produced by *National Scientific and Research Institute for Physical Technical and Radiotechnical Measurements, JINR Dubna, Russia*). TVO series are temperature resistors made of carbon-ceramic composites, about 4%, 50 - 200 Angstrom carbon, aluminum oxide powder (~ 90%), boron &lead flux, ageing for seven years at the room temperature. Then they are treated by twenty times thermal cycling in the range from 77.4 to 373 K.TVO sensors have zero inductance and high resistance of the electrical insulation - up to 5000 Mohm. Specific characteristics are shown in figure 1 where R_0 = 1000 Ω at 300K [12].

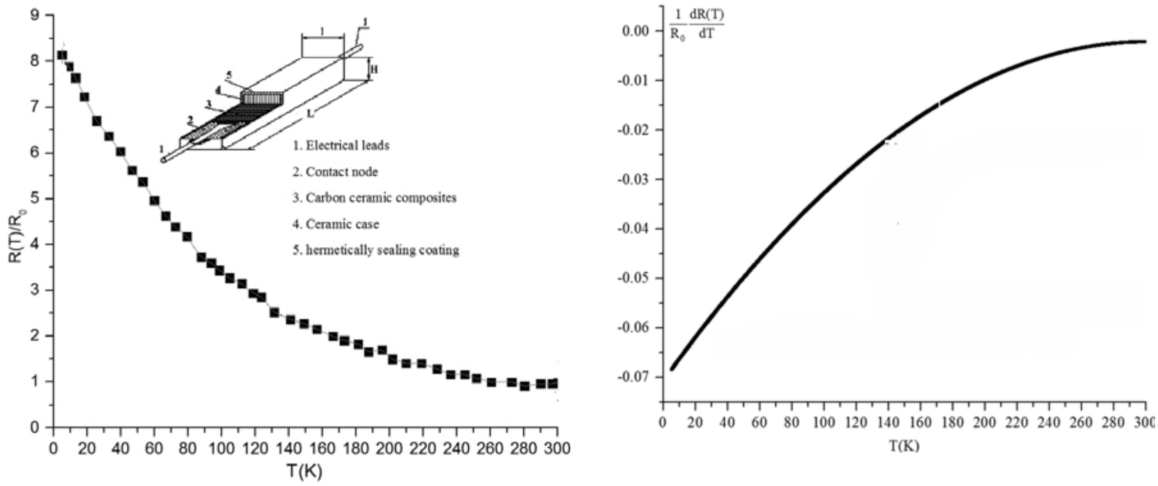


Fig. 1.TVO- Temperature resistor characteristics(a) and TCR (b)

Temperature coefficient of resistance (TCR) for TVO (figure 1b) has a polynomial behavior:

$$TCR=\frac{1}{R_0}\frac{dR(T)}{dT}=-0.07508+4.56426\times10^{-4}T-7.59805\times10^{-7}T^2 \quad (1)$$

Experimental set-up

Sensor 1: Solution of ~8% (wt)SWCNT in THF, ultrasonication for 5h at room temperature to disperse the carbon nanotubes. 20μL from solution was drop casted on the electrodes and applied 7000V/m between the two silver electrodes for 1min.

Sensor 2: 10 ml of 5% Nafion was diluted with 25 ml solution prepared for sensor 1, sonication 20min. 20 μLfrom solution was drop casted on the electrodes and applied 7000V/m, 1min, to let nanotubes for self-alignment. This method is similar with dielectrophoretic deposition [13].

Both sensors are drying at 70^0C for 2h, over coated with 5% Nafion solution as protective layer with drying in the same conditions. The sensors are assembled on copper block figure 2 a. The measurements are performed with data acquisition system (National Instruments Field Point acquisition, FP-AI-110), figure 2b. The electrical resistances are measured using four points method at constant current, 0.1mA.

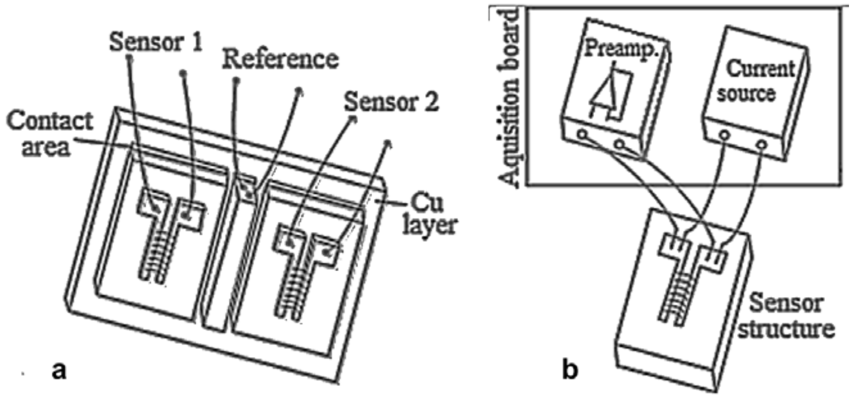


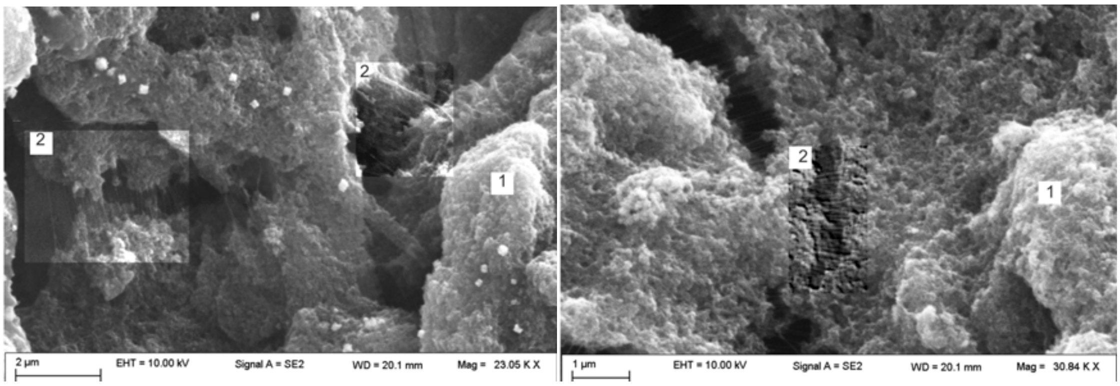
Fig 2.Experimental set-up.a) The two sensors and the reference, TVO 207, assembled on the copper block. b) Four point connection and the acquisition board for each single sensor.

Morphological and topography analysis: Scanning electron microscopy (FESEM VP, CARL ZEISS, with a resolution of 0.8 nm at 30 kV and 2.5 nm at 30 kV in VP mode; magnification up to 1.000.000X).

3. Results and discussions

3.1 Scanning electron microscopy (SEM)

SEM images in Fig. 3 reveal several features related to the alignment of the carbon nanotubes in the structure of the two sensors.



a b

Fig. 3. Microstructure of the drop casted carbon nanotubes deposited on: a) Sensor1 b) Sensor 2. In inset 1- Nafion films, 2- details of the nanotubes wires aligned in electrical field (7000 V/m)

The alignment of CNTs from solutions is quite different. CNTs drop casted from THF are drawn from bundles. The structure is made of network of bundle nanotubes interconnected by nanotubes wires (sensor 1, inset 2). In sensor 2 the alignment of CNTs in presence of Nafion solution takes place in small regions. Nafion, after electric field releasing, shrink in small domains and hamper tube wire alignment on large dimensions (figure 2b, inset 2). In both figures, Nafion, over coating layer, is indexed with 1. Even though the sonication time was large enough the CNTs are still not well separated. In addition, THF (protic, polar heterocyclic solvent with high dielectric constant) and high surface tension is not enough to unbundle CNTs and need other more efficient solvent combination. In figure 3b the Nafion polymer plays a negative effect by shrinking CNTs in very small regions, hampering the alignment in electrical field.

3.2 R-T characterization

Both sensors are aged by repeated cooling and heating cycles, from room temperature to the liquid nitrogen temperature, until resistance reaches constant value with error less than 1%. After ageing, the specific resistance measurements are shown in figures 4. The resistances at 273K: R_{01}=554Ω (sensor 1) respective, R_{02}=1164 Ω (sensor 2). The plots, R/R_0 - T are quasi-linear in the temperature range of 190 K ÷ 300 K thus suggesting that the electrical contacts between carbon nanotubes and the metal electrodes have an ohmic behavior, in agreement with other reports [8,14].

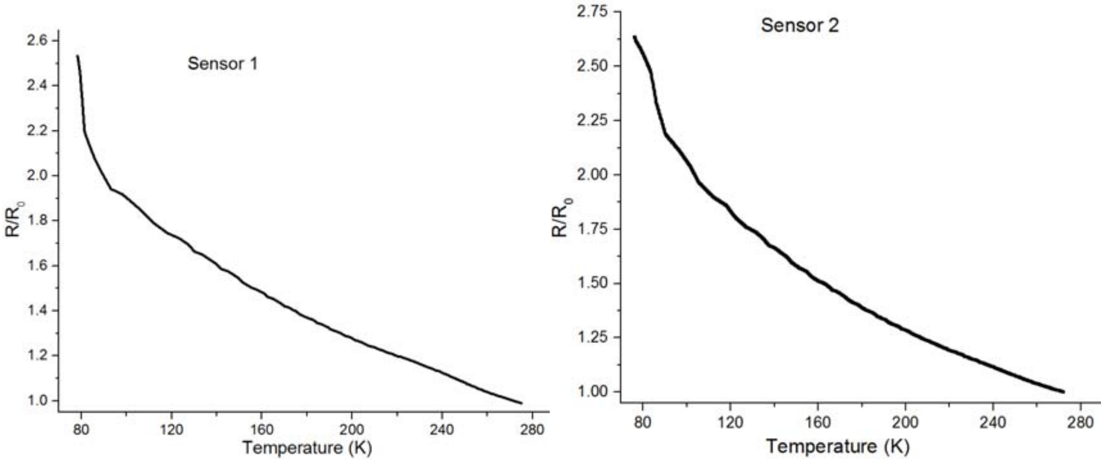


Fig. 4.The specific resistance R vs temperature for Sensor1 and Sensor2.
Normalized R-T curve of the two sensors; R_{273}: 554 Ω for Sensor 1 and 1163 Ω for sensor 2.

For applications purpose and integration in electronic devices, both plots can be parameterized. In the range 190 K ÷ 300K the sensors have linear behavior in agreement with other reports using CNTs for nanosensors [**Error! Bookmark not defined.**] and can be parameterized as:

$$R(T) = p_1 T + p_2 \quad (2)$$

In the temperature range 77 K ÷ 190 K the resistances are fitted with exponentials:

$$R(T) = a e^{bT} + c e^{dT} \quad (3)$$

The coefficients from (2) and (3) (table1) are estimated for two different run tests (initial and after 50 runs) during heating/cooling cycles after ageing.

By comparison with sensors based on carbon-ceramic composites (figure 1), sensors 1 and 2 have different behavior and cannot be characterized by a polynomial TCR. Usually, carbon- ceramic composites are made of fine dispersion of carbon particles in a ceramic matrix with concentration over percolation threshold [15, 16] and the carbon materials govern the electrical resistance.

Table 1.The fitting parameters of the experimental data for sensor 1 and sensor 2

		Linear region				Exponential region			
		p_1	p_2	R^2	a	b	c	d	R^2
Sensor 1	Run test1	-2.391	1247	0,9983	$3.51\cdot10^{12}$	-0.2963	1704	-0.004087	0.9955
	Run test 50	-2.402	1248	0,9975	$6.718\cdot10^{6}$	-0.1310	1716	-0.004068	0.9984
Sensor2	Run test 1	-5.053	2634	0,9969	$3.188\cdot10^{7}$	-0.1405	3850	-0.004388	0.9973
	Run test 50	-5.098	2637	0,9956	$5.555\cdot10^{4}$	-0.0586	3697	-0.004137	0.9977

TCR in TVO has the conduction mechanisms specific for a carbon- composite materials. The specific resistance increases with temperature from room temperatureto77K, the liquid nitrogen temperature. For sensors 1 and 2, the structures are made of small regions of bundled CNTs interconnected with CNTs wires, aligned in electric field. The thermal behavior will be dependent of type of nanotubes (metallic & semiconductor composition), electrical contacts with Ag, ambipolar conduction [**Error! Bookmark not defined.**], and polymer solution for stabilization during cooling (strongly dependent of glass transition and brittleness). In figure 5, are shown the plots for both structures based on general assumption that resistance for CNTs is dependent of activation energy:

$$R_s = R_0 \exp\left(\frac{E_a}{kT}\right)$$

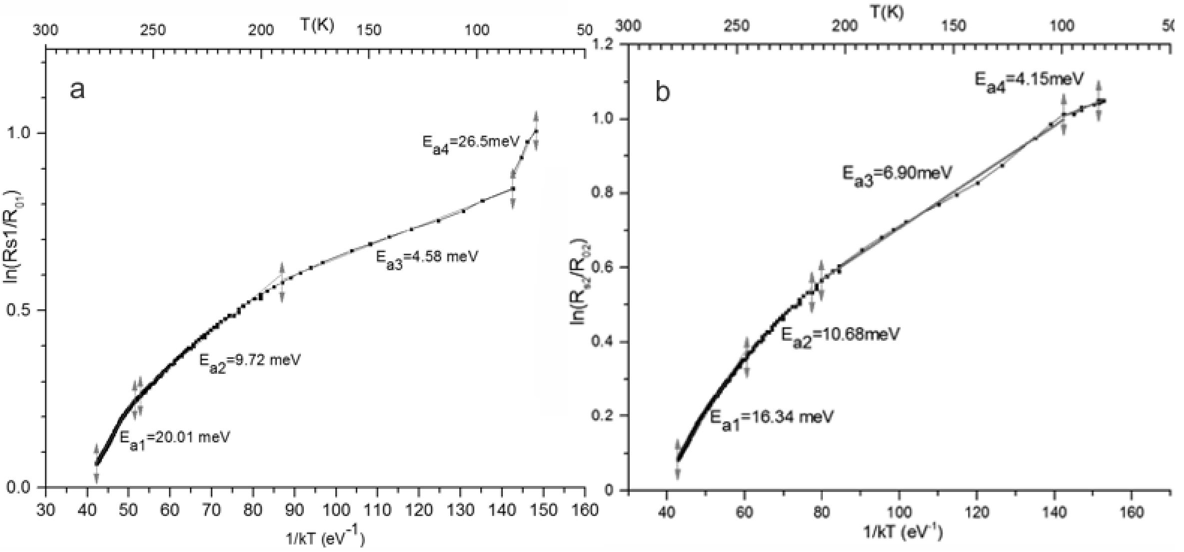


Fig. 5. The activation energy of the CNTs for both structures, sensor 1 (a) and sensor 2 (b)

Roughly, each plot is approximated in four linear regions with specific activation energy from 20 meV to 4 meV. The last activation energy (figure 5a) is not in agreement with continuous temperature decreasing. The first assumption is the loss of the electrical contact between nanotubes with the silver electrodes. The polymer, the over coating layer, brings an improvement in stability (figure 5 b). Appropriate coatings with non-brittle polymer films, assures a good stability for contacts terminal electrodes-carbon nanotubes, reduce possible mismatches at the device interfaces [17]. Also, addition of polymer bond in dropcast solution (in this case Nafion) increases the mechanical stability: the contacts between CNTs and with the terminal electrodes. The differences between activation energies are assigned of the CNTs compositions, which is heterogeneous in the content of semiconducting and metallic components in raw material. The conduction mechanisms are dependent of percentage of semiconducting and metallic nanotubes. If the thermal energy is higher than the activation energy (>20meV), the conduction mechanisms are not dependent of carbon nanotubes chirality and relation (2) is valid. At low temperature (<190K, E_a< 7 meV) the conduction mechanisms are quite dependent of chirality and of percentage of semiconducting carbon nanotubes. In the low temperature range, metallic CNTs are dominant. Simultaneous takes place depletion in charge carriers and controversial issues in carbon behavior at low temperature where resistance increases. This is not the usual one that one expects for metals or semimetals and can be understood within the usual electron–phonon interaction mechanisms [18]. In designing microsensors for temperature measurements with carbon nanotubes the major drawbacks encountered are the electrical contacts between nanotubes with the terminal electrodes and the heterogeneous composition. Both induce hysteresis and longtime cycling for ageing. The temperature variations during heating-cooling cycles induce possible mismatches at the device interfaces [**Error! Bookmark not defined.**]. In the range 77K-300K (domain that was used in our experiments) corresponding to a slow heating-cooling cycles, have proved a good reproducibility, and low hysteresis for R(T) of about-0.309%/°C (figure 6).

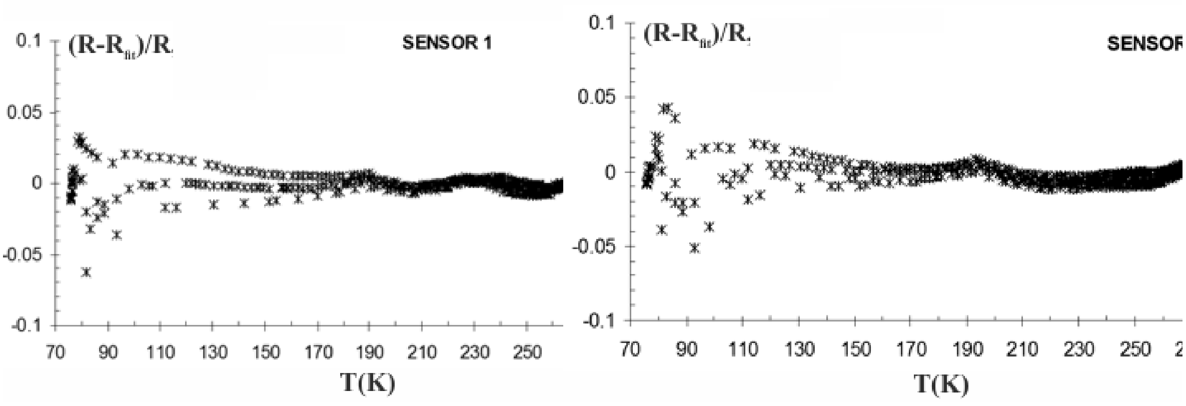


Fig. 6-Reproducibility between the experimental results and the fitted resistance of the sensors structures (curves fitted with equation 2 and 3)

That is in agreement with the results reported in [19] for CNTs thick films (30-40 μm). Both sensors (figure 4) have the sensitivity coefficient ($S=\Delta R/(R\Delta T)$ at 20°C around of -0.24%/°C. The temperature sensitivity reported with carbon nanotubes was found to be higher than those based on hydrogenated multi-wall carbon nanotubes (-0.16%/°C) [20], carbon nanotube films deposited on diamond crystals (-0.14%/°C) and carbon - polymer sensors (-0.13%/°C) [**Error! Bookmark not defined.**]. This means that the role of the substrate and nanotubes film processing technology respective, the nanotubes density have an important influence on the sensor performances [21]. The hysteresis is quite insignificant. During heating-cooling cycles the resistance of each sensors return to close initial value at room temperature. The resistance of the both sensors returns to the same values after a succession of cooling cycles followed by a rapid heating (blowing with hot air source).

4. Conclusions

In the cryogenic field, the sensors based on carbon nanotubes are dependent of chirality, concentration of nanotubes, the polymer materials for coating and stabilization.

The resistance is quite dependent of ratio semimetallic / metallic carbon nanotubes that exist in the dropcast solution. The resistance is sensitive to the activation energy. By comparison with carbon-ceramic resistors, the sensors based on CNTs have a high sensitivity with linear behavior in the range 190K- room temperature appropriate for integration in electronic on plastic devices.

In the range 190K down to 77K a bi-exponential equation is more convenient for approximation being direct related with the activation energies and concentration of metallic CNTs respective, with the charge carriers depletion.

The drop cast from appropriate solvents and dielectrophoretic alignment is a simple and friendly method to design microsensors based on CNTs.

Acknowledgement

The financial support of Romanian Grants PN-II-ID-PCE-2011-3-0815 - contract no 64/2011, the Sectorial Operational Programme Human Resources Development (SOP HRD), financed from the European Social Fund and by the Romanian Government under the contract number SOP HRD/107/1.5/S/82514,

References

[1] H. Preston-Thomas, The International Temperature Scale of 1990 (ITS-90) Metrologia **27**, 3 (1990)
[2] P. R. N. Childs, J. R. Greenwood, C. A. Long, Review of scientific instruments, **71**(8), 2959 (2000)
[3] S. Iijima, Nature **354**,56-58 (1991)
[4] Marinobu Endo, M.S. Strano, P.M. Ajayan, Topics in Applied Physics, **11**, 13 Springer 2008
[5] J.Kong, N. R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Science **287**, 622(2000)
[6] A.Di Bartolomeo, M.A. Sarno, F. Giubileo, C. Altavilla, L. Iemmo, S. Piano, F. Bobba, M. Longobardi, A. Scarfato, D. Sannino, A. M. Cucolo, P. Ciambelli, Journal of Applied Physics **105**, 064518, (2009).
[7] S.J. Tans, A.R.M. Verschueren, C. Dekker, Nature, 49 (1998)
[8] C.Y. Kuo, C.L.Chan, C.Gau, C.-W.Liu, S.H. Shiau, J.-H. Ting, IEEE Trans on Nanotechnology, **6**(1) 63 (2007)
[9] Y.-K. Kwon, P. Kim, Unusually High Thermal Conductivity in Carbon Nanotubes, High Thermal Conductivity Materials, Springer, New York, 227 (2006)
[10] M.S. Dresselhaus, G. Dresselhaus, R. Saito, Carbon, **33**(7), 883(1995)
[11] P. L. McEuen, M. S. Fuhrer, H. Park, IEEE Transactions on Nanotechnology **1**, 78 (2002).
[12] V.I. Datskov, J.G. Weisend II, Cryogenics, 34, suppl 1, 425 (1994)
[13] C.K.M. Fung, Wen J. Li, Dielectrophoretic batch fabrication of encapsulated carbon nanotube thermal sensors, Asia-Pacific Conf. of Transducers and Micro-Nano Technology (2004)
[14] R. Martel, V. Derycke, C. Lavoie, J. Appenzeller, K.K. Chan, J. Tersoff, Ph. Avouris, Phys Rev Lett, **87**(25), 256805-1-4 (2001)
[15] J. Yliostalo, P. Berglund, T.O. Niinikoski, and R. Voutilainen, Cryogenics **36**, 1033 (1996)
[16] Akira Kishimoto , YutoTakagawa, Takashi Teranishi, Hidetaka Hayashi, Materials Letters **65**, 2197 (2011)
[17]A.M. Zaitsev, A.M. Levine, S.H. Zaidi, Phys. Status solidi, **204**(10), 3574 (2007)
[18] N Garcia, P Esquinazi, J Barzola-Quiquia, S Dusari, New Journal of Physics **14**,053015-1-14 (2012)
[19] KH. S. Karimov, F. A. Khalid, M. Tariq Saeed Chani, A. Mateen, M. Asif Hussain, A. Maqbool, Optoelectronics and Advanced Materials – Rapid Communications, **6**(1-2), 194 (2012)
[20] V. Kumar, A.A. Bergman, A.A. Gorokhovsky, A.M. Zaitsev, Carbon, 49(4) 1385 (2011)
[21] S.S. Courts, P.R. Swinehart, in Advances in Cryogenic Engineering, **45**, 1841 Kluwer-Plenum Press, New York, 2000