BULLETIN OF THE POLISH ACADEMY OF SCIENCES TECHNICAL SCIENCES, Vol. 62, No. 4, 2014 DOI: 10.2478/bpasts-2014-0082

Flexible, textronic temperature sensors, based on carbon nanostructures

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Abstract. The paper presents a comparative analysis of two types of flexible temperature sensors, made of carbon-based nanostructures composites. These sensors were fabricated by a low-cost screen-printing method, which qualifies them to large scale, portable consumer electronic products. Results of examined measurements show the possibility of application for thick film devices, especially dedicated to wearable electronics, also known as a textronics. Apart from general characterisation, the influence of technological processes on specific sensor parameters were examined, particularly the value of the temperature coefficient of resistance (TCR) and its stability during the device bending.

Key words: textronics, flexible temperature sensors, flexible electronics, smart textiles.

1. Temperature sensors in textronics

Temperature is one of the most substantial parameters for diagnostics and human body monitoring. For this reason it is one of the most frequently controlled signal, measured by different kinds of sensors, in innovatory medical, protective and military smart textiles [1-3]. The human body temperature should be controlled, because its rise, caused by a serious illness, or an external heat flow, may easily lead to hyperthermia, which results in weakening, nausea, dizziness, and blood pressure increase. This in an extreme situations may cause consciousness disturbances, coma or even death [4]. Therefore, the full integration of the temperature sensors in medical and protective smart suits is becoming more and more necessary towards higher functionality and better protection of these product consumers [5]. Textronic sensors should be characterized by a good quality and precision and also a high flexibility, light weight, a high endurance and resistance to mechanical damage, as well as resistance to humidity (sweat, washing) and atmospheric conditions (changeable temperature, rain, salt) [6]. These requirements are quite demanding and sometimes it is difficult to meet them all using noncommercial structures. Therefore, typically, textronic devices are produced on the basis of commonly available miniaturized electronic circuits and sensors based on semiconductors, thermo-resistive non-organic materials or even thermocouples. However most of these constructions appeared to be not adequate for that kind of application, because of their stiffness, complication conversion systems or insufficient encapsulation. The presented paper shows the idea of flexible sensors fabrication, which can be used to measure the body temperature in the smart textiles, in the active range of 30–43°C. Elaborated devices were produced on the basis of resistance change mate-

All mentioned parameters are critical in terms of designed textronic applications, in which mechanical bending stress is one of the most common endanger. Accuracy, stability of the results and linearity of characteristics, accompanied by high dynamics owing to low thermal resistance, should be combined with proper flexibility and endurance.

2. Carbon nanostructures in flexible applications

Carbon nanostructures are nowadays the scope of many research programs owing to their unique mechanical, optical and electrical parameters. An important group of these materials consists of various types of carbon nanotubes (CNT). These structures are constructed as cylinders formed by single (SW-CNT) or multiplied concentric (MWCNT) cylinders made of graphene layers. Among exceptional properties of CNT material one may enumerate extremely high stretching resistance, as high as 63 GPa with density of only 1.3–1.4 g/cm³, very low electric resistance and high heat conductivity of 6000 W/mK along the tube length [8, 9]. Moreover, extremely high mechanical flexibility of cured composites based on CNTs material was also observed, which gave the prompt for authors practical experiments. Apart from SWCNT, which are typically superb according to their parameters, but also more expensive in the production process, the cheaper Multi Walled Nanotubes middle group – Double Walled Nanotubes (DWCNT), presented in Fig. 1, may be obtained. It is important to note,

rial – a special Multi-Wall Carbon Nanotube (MWCNT) layer. Obtained elements are characterized by a negative TCR, small inertia, and linearity of the temperature-resistance characteristics in the whole measurement area and most importantly by independence on mechanical bending [7].

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that due to high anisotropy of parameters the pre-processing functionalization of the nanotube material is widely postulated, however practical, inexpensive methods of this treatment are still under elaboration.

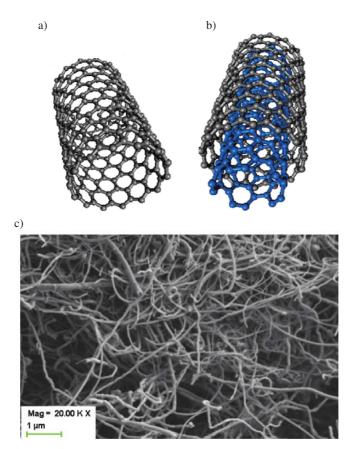


Fig. 1. SWCNT (a), DWCNT (b) and HRSEM picture of MWCNT (c) after Refs. 10, 11

Thanks to their promising parameters CNTs were added as the components to some materials, enhancing their mechanical parameters, thermal or electrical conductivity [12–14]. This material was also used in many flexible electronics and textronics smart systems [15, 16] and standard sensors [17] along with other carbon nanostructures [18]. These successful applications encourage authors to continue research on thermo-sensitive layers fabrication, based on the new CNTs materials through the development of previous soot-polymer tests [3].

3. Experimental printed sensors

Temperature sensors were fabricated on flexible polyimide by screen-printing technology, which is cheap, popular, scalable and widely utilized for industrial production [6]. Although new printing-based techniques as inkjet printing, flexography or gravure offer more precision in shape mapping, screen printing technique still prevails in mass-production and industrial applications. This is particularly evident in thick-layer electronics, especially in the production of: different kind of sensors, resistors, heaters, hybrid and multi-layer circuits [19].

This technique was also previously utilized by authors in flexible applications, like flexible sensors and photovoltaic fabrication [3, 20]. Owing to possibility of adaptation to flexible substrates, such as foils, paper or even textiles, these devices may be also easily implemented into the fabric structures.

Considering unique features of MWCNT, this material was chosen as a main component of the temperature sensors active area. The thermo-sensitive layer was screen-printed using a composition, consisted of poly (methyl methacrylate) (PM-MA), organic solvent, and CNTs, as a functional conductive phase with organic resin filler [21, 22]. The biggest challenge was to fully disperse CNTs in the resin because CNTs tend to form clusters and groups. To obtain proper, uniform structure prior to printing composed paste was stirred in the ultrasonic chamber and smoothed in the roll-mill, according to carbon-based paste preparation procedure [6]. After screen-printing phase the obtained sensors were thermally cured, to obtain flexible, stable layers. In the experiments two various CNTs content (0.25% and 1%) were tested for initial resistance and temperature coefficient regulation.

As a substrate the polyimide high-temperature 75 μ m KAPTON® HN foil was chosen. This material was previously verified by the authors in mid-temperature layer formation processes up to 430°C [20]. Additionally it is characterized by a high flexibility, moderate elongation, and small thermal expansion coefficient [23].

In the first step of the temperature sensors production the device contacts were fabricated on the metallized KAPTON® foil, the 35 μ m gold-plated copper layers were obtained, using anodizing method for gold layer deposition. The gold layer was added to provide a better oxidation protection and reduction of contact resistance. The full structure of printed MW-CNT sensors (a) as well as a contact cross-section (b) and a real device photo (c) are presented in Fig. 2.

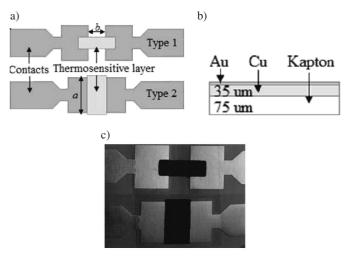


Fig. 2. The schematic of sensor structure (a), contact cross-section (b), final devices (c)

For proper thermal characteristics of manufactured sensors, and adjustment of their initial resistance special dual time-temperature profile of paste stabilization was elaborated.

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It contained two 1 hour heating processes in 120°C , separated by cooling until room temperature. This treatment allowed for linear and fully stabile sensors characteristics. Subsequently the elements were encapsulated by high mechanically proof sticking tape by 3M company. Thanks to this process mechanical and humidity resistant sensors with negative TCR and linear characteristics were obtained. Physical parameters of manufactured elements are presented in Table 1, where d marks the thickness of obtained layers, a – the width, b – the length, R_{30} – the reference resistance value in the temperature 30°C , ρ – the resistivity of the material, and R_{\square} – sheet resistance. All values were determined as an arithmetic average of a series of 12 samples. Resistance deviation varies from 0.5% for 1^{st} sensor type with 0.25% of CNT content to 12% for 2^{nd} sensor type with 1% of CNT content.

Table 1 Parameters of manufactured sensors

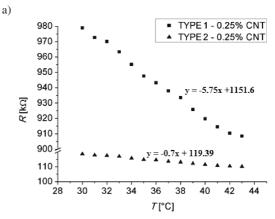
Sensor type	d [μ m]	a [mm]	b [mm]	R_{30} [k Ω]		R_{\square} $[\Omega/\square]$	TCR [ppm/K]
Type 1 (1% CNT)	12 -	3	4	120	1.1	90105	-1436
Type 2 (1% CNT)		9	4	15	0.4	33368	
Type 1 (0.25% CNT)	6 -	3	4	979	4.4	734213	-847
Type 2 (0.25% CNT)		9	4	119	1.6	266985	

It was observed that the increase of MWCNT content as well as the layer width leads to the decrease of the initial resistance value, however this dependence is non-linear in both mentioned cases (i.e. four times higher CNTs content resulted in 80% resistance drop). Consequently by paste composition and geometric sensor correction the R_{30} value can be easily adjusted to the A/D conversion circuit needs.

4. Results and discussion

Twelve series of both types of manufactured sensors were tested according to their thermo-resistance parameters. For their characterization a measurement setup, based on an isolated calorimeter, was constructed. This system was equipped with an on-line data collection digital mulitimeters: BM 857, coupled with PC computer by optical RS-232 port and RIGOL DM3062, recording the results by USB port. Sensor characteristics were collected in the human skin temperature range 30–43°C, with 1°C interval. Full device characteristics for all sensor types are presented in Fig. 3, where average values for examined series are shown.

One can notice the stabile, negative temperature coefficient and good linearity of the characteristics with variation smaller than 5% in the whole measurement area. What is also important, obtained values are do not dependent on the initial resistance. However, for the textronic application investigated sensors must also present high flexibility without significant impact on their thermo-electric characteristics. For this goal obtained elements were tested in dynamic bending cycles. During the tests all manufactured elements were bent at 90° angle with the frequency of 2 Hz for more than 120 s. The dynamic resistance changes were collected and stored. The results of conducted tests are presented in Figs. 4 and 5.



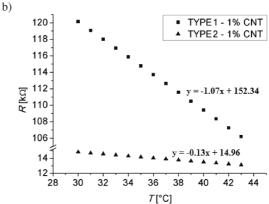
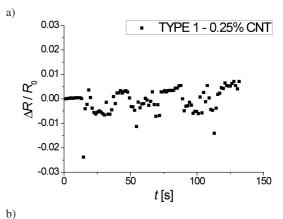


Fig. 3. Thermal-resistance characteristics of obtained sensors with 0.25% CNT content (a) and 1% CNT content (b)



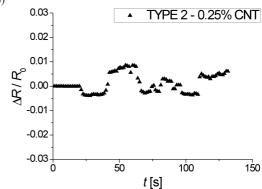
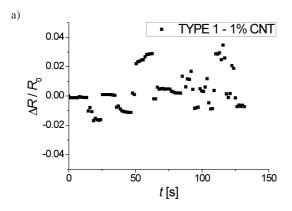


Fig. 4. Dynamic resistance change of sensor with 0.25% CNT content

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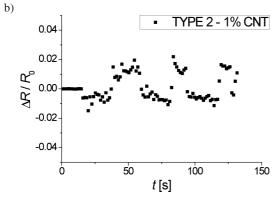


Fig. 5. Dynamic resistance change of sensor with 1% CNT content

For both sensor groups no noticeable influence of bending stress on the element resistance was detected (mid value of resistance change smaller than 0.25%). Experimental results confirmed the high flexibility and durability of nanotube layer. Better stability is observed for sensors with 0.25% CNT content.

5. Summary and conclusions

As the result of reported investigation fully flexible temperature sensors on foil stripes, for textronic applications were produced. All obtained elements presented linear temperatureresistance characteristics in the whole range of human body temperature with the relatively high, stabile, negative thermal coefficient. Those features recommend elaborated elements for human diagnostic and protection circuits. Additionally extremely high resistance to bending influences on resistance characteristics, and cheap, robust construction designates them for the textronic applications. Two possibilities of the initial resistance regulation for the converter circuit needs were proposed and positively verified. The implementation of CNTs based paste in the role of thermo-active layer appeared innovative and very effective in elimination of bending influence on sensor detection, what is the real problem in the case of traditional graphite and soot based elements. The presented work also shows the possible future utilization of traditional screen-printing technology in smart textiles application.

It is important to note that obtaining the designed, stabile parameters of the sensor demands not only proper paste composition and screen-printing regime, but also specific postthermal treatment. In the future work authors plan to expand the current investigation for the textronic sensors of other physical parameters, such as pressure, humidity etc. Also a proper, flexible encapsulation method, based on an organic layer deposition is a critical problem in the scope of the research conducted by the authors.

REFERENCES

- [1] R. Paradiso, G. Loriga, N. Taccini, A. Gemigani, and B. Ghelarducci, "WEALTHY a wearable healthcare system: new frontier on e-textile", *J. Telecom. and Information Technology* 4, 105–113 (2005).
- [2] K. Gniotek, J. Gołębiowski, and J. Leśnikowski, "Temperature measurements in a textronic fireman suit and visualization of the results", *Fibres & Textiles in Eastern Europe* 17 (1), 97–101 (2009).
- [3] S. Bielska, M. Sibinski, and A. Lukasik, "Polymer temperature sensor for textronic applications", *Material Science & Engineering* B 165 (1–2), 50–52 (2009).
- [4] A. Bonfiglio and D. De Rossi, *Wearable Monitoring Systems*, Springer, New York, 2011.
- [5] M. Jakubowska and J. Sitek, *Printed Electronics in Poland*, pp. 156–167, Tele and Radio Research Institute Publisher, Warszawa, 2010, (in Polish).
- [6] S. Walczak, Intelligent Textiles International Developments in Textronics, pp. 99-115, New paradigm of technological innovations, Acta Innovations, Łódź, 2012.
- [7] S. Bielska, "Comparison of flexible temperature sensors parameters, based on polymeric and carbon nanotube paste", Microtherm 2009 Conf. M aterials 1, CD-ROM (2009).
- [8] Min-Feng, "Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load", *Science* 287, 637–640 (2000)
- [9] P.G. Collins and P. Avouris, "Nanotubes for electronics", *Scientific American* 283 (6), 62–69 (2000).
- [10] Y.L. Zhao and J.F. Stoddart, "Noncovalent functionalization of single-walled carbon nanotubes", *Acc. Chem. Res.* 42 (8), 1161–1171 (2009).
- [11] M. Słoma, "Polymer composites with carbon nanotubes for printed electronics applications", XII Int. PhD Workshop OWD 1, 437–442 (2010).
- [12] M. Sibiński, Z. Lisik, D. Sęk, and A. Iwan, "Novel construction of CdTe solar cell based on polyketanil structure", *Materials Science and Engineering B-Advanced Functional Solid-State Materials* 165 (1–2), 71–73 (2009).
- [13] I.A. Guz and Y. Rushchitskii, "Comparison of mechanical properties and effects in micro- and nanocomposites with carbon fillers (carbon microfibers, graphite microwhiskers, and carbon nanotubes)", *Mechanics of Composite Materials* 40 (3), 179–190 (2004).
- [14] C. Berger, Y. Yi, Z.L. Wang, and W.A. de Heer, "Multiwalled carbon nanotubes are ballistic conductors at room temperature", *Appl. Phys.* A 74, 363–365 (2002).
- [15] H. Sirringhaus, "High-resolution inkjet printing of all-polymer transistor circuits", *Science* 15, 290 (5499), 2123–2126 (2000).
- [16] F. Axisa, A. Dittmar, and G. Delhomme, "Smart clothes for the monitoring in real time and conditions of physiological, emotional and sensorial reactions of human", *Proc. 25th Annual Int. Conf. IEEE* 4, 3744–3747 (2004).

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Flexible, textronic temperature sensors, based on carbon nanostructures

- [17] T. Pustelny, "The sensitivity of sensor structures with oxide graphene exposed to selected gaseous atmospheres", *Bull. Pol. Ac.: Tech.* 61(3), 705–710 (2013).
- [18] T. Pustelny, M. Setkiewicz, S. Drewniak, E. Maciak, A. Stolar-czyk, M. Urbańczyk, M. Procek, K. Gut, Z. Opilski, I. Pasternak, and W. Strupinski, "The sensibility of resistance sensor structures with graphene to the action of selected gaseous media", *Bull. Pol. Ac.: Tech.* 61 (3), 293–300 (2013).
- [19] R. Loasby, J. Savage, and J Holmes, *Handbook of Thick Film Technology*, Electrochemical Publication LTD, Edinburgh, 1976.
- [20] M. Sibiński and Z. Lisik, "Polycrystalline CdTe solar cells on elastic substrates", Bull. Pol. Ac.: Tech. 55 (3), 287–292 (2007).
- [21] A. Łukasik and S. Nowak, "Relaxation of stress in polymercarbon microcomposite resistive layers", XXX IMAPS – Conf. Materials, Imaps, Cracow, Poland, 2006.
- [22] M. Jakubowska, M. Sloma, and A. Mlozniak, "Polymer composites based on carbon nanotubes for printed electronics", 32nd Int. Spring Seminar on Electronics Technology, Conference Materials 1, 1–5 (2009).
- [23] http://www2.dupont.com/Kapton, access on 01.03.2013.

Bull. Pol. Ac.: Tech. 62(4) 2014 763