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LAYERS WITH THE TENSORESISTIVE PROPERTIES AND THEIR POSSIBLE APPLICATIONS IN MEDICINE

L.P. Ichkitidze[1,2]*, A.Yu. Gerasimenko[1,2], V.M. Podgaetsky[1], S.V. Selishchev[2]

[1]National Research University of Electronic Technology,

bld. 1, Shokin Square, Zelenograd, Moscow, 124498, Russia

[2]I.M. Sechenov First Moscow State Medical University,

bld. 4, Bolshaya Pirogovskaya Str., 2, Moscow, 119991, Russia

*e-mail: ichkitidze@bms.zone

Abstract. Layers of different materials, including nanocomposites, containing carbon nanotubes, with the tensoresistive properties are discussed. The investigated layers are divided into two groups: without (group I) and with carbon nanotubes (group II). A group-I material that is the most suitable for fabrication of a tensoresistor is the elastomer with microchannel, filled with a conductive liquid. In group II, these are the (0.2 – 10)-μm-thick layers consisting of the carboxymethylcellulose matrix, filled with multiwalled carbon nanotubes (~5 wt.%). The investigated layers can be used as alternative tensoresistors for medical applications.

Keywords: carbon nanotubes; carboxymethylcellulose; nanocomposite layer; tensoresistor.

1. Introduction

In medicine, it is often necessary to control limb, joint, chest, thorax, hydrops, tumors etc. movements and soft tissue strain, e.g., during post-surgery recovery. This is made using various strain gauges. The simplest and most wide-spread strain gauges are based on the phenomenon of resistance variation under strain and called tensoresistors. The strain sensitivity of these devices is determined as $S = \delta R/\varepsilon$, where $\delta R = \Delta R/R_0$, R_0 is the initial resistance, ΔR is the absolute resistance variation under strain, $\varepsilon = \Delta l/l$, l is the initial length of a sensitive element, and Δl is the absolute variation in its length.

Conventional tensoresistors are fabricated from metal or semiconductor materials. Meander-shaped tensoresistors formed from a metallic foil have the low temperature resistance coefficient ($\alpha \leq 10^{-5}\,K^{-1}$) and relatively wide strain measurement range ($\varepsilon = \pm 5$ %), but the low strain sensitivity ($S \leq 10$). Semiconductor tensoresistors are characterized by the high sensitivity ($S \sim 100 - 200$), very low strain ($\varepsilon \leq 0.2\%$), and high temperature resistance coefficient ($\alpha \geq 10^{-3}\,K^{-1}$) [1]. Note that both the metal and semiconductor tensoresistors have insufficient elasticity and strongly restrict movements of a biological object, because their moduli of elasticity E exceed the value characteristic of a human skin by several orders of magnitude ($E \sim (25 - 220)$ kPa, $\varepsilon >> 1$ %) [2].

In this work, we briefly describe different layers with the tensoresistive properties (hereinafter, tensoresistors) that were designed using original methods and/or materials and their potential applications in medicine. The investigated devices are divided into two groups. Group I is formed from the tensoresistors that do not contain carbon nanotubes (CNTs) and group II, from the tensoresistors, containing CNTs or based on nanocomposites with CNTs.

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2. Layers – Group I

A great number of tensoresistors have been developed and fabricated using nanoparticles and nanotechnologies. However, the high strain sensitivity ($S \geq 100$) is often attained in a very narrow strain range ($\varepsilon \leq 1$ %), which is not suitable for medical applications. Indeed, to control movements of human body parts, a strain of $\varepsilon \geq 10$ % is usually required. In [3], the materials, based on ZnO nanowires characterized by $S \approx 1250$ and $\varepsilon \leq 1$ %, were reported. In a hybrid material, consisting of ZnO nanowires, fixed on polysterene nano- and microfibers, the high ε values ($\leq$ 50 %) and relatively low S values (~100) were established [4]. A tensoresistor is encapsulated in a polydimethylsiloxane (PDMS) film and has the high moisture resistance. However, the excessively high resistance ($\geq 10^9$ Ω) and, consequently, high intrinsic noise level of the material significantly restrict the strain measurement accuracy.

The parameters $S \sim 10$ and $\varepsilon \sim (20 - 80)$ % were obtained in a tensoresistor, based on the thermoplastic elastomer, containing ~50 mass.% of soot [5]. The proposed sensor, however, rapidly loses its strain sensitivity ($S \leq 0.1$) at $\varepsilon \leq 10$ % and can probably be used to detect fabric strain.

The graphite layers deposited onto natural rubber substrates exhibit the tensoresistive effect with the high parameters: $S \sim 12 - 346$ and $\varepsilon \leq 246$ % [6]. Nevertheless, their $\delta R(\varepsilon)$ dependences are strongly nonlinear, especially in the range of $\varepsilon \geq 100$%. The strong nonlinearity of the $\delta R(\varepsilon)$ dependence is caused mainly by the behavior of pure rubber, i.e., by the strong nonlinearity of the stress induced during straining the rubber. Hence, the use of such layers as tensoresistors is complicated by the difficulty of brining the $\delta R(\varepsilon)$ curves to the linear shape with good accuracy.

In [7], an original tensoresistor consisting of a silicon elastomer with microchannels filled with a conductive liquid was developed to control movements of different human body parts. The strain (tension) increases the length and decreases the width of a microchannel and, thus, leads to the corresponding increase in its resistance. Testing of the tensoresistor showed that it has a strain of $\varepsilon \leq 300$ % and a sensitivity of $S \leq 3$ at bending angles of $\theta < 120°$; the strain measurement error was ~ 8 %. Obviously, this sensor is inapplicable to detecting movements of human body parts, where the angles can be in the range of $\theta \geq 120°$, e.g., in total finger, knee, or elbow flextions.

3. Layers – Group II

Carbon nanotubes (CNTs) have the unique properties, including high strength, heat and electric conductivity, and optical transparency. Nanocomposites with even minor (< 10 %) CNT additions acquire special characteristics. Depending on a fabrication technique used and nanomaterial composition, the tensoresistive effect in the CNT-based layers is either enhanced or suppressed. Indeed, the layers consisting of multiwalled CNTs (MWCNTs) added with $AgNO_3$ in a concentration of 2 – 10 g/l, deposited onto PDMS substrates, exhibit a stable resistance upon multiple bending in the angle range from −180° to +180° and have almost no tensoresistive properties [8].

Study of the MWCNT films, used as tensoresistors, showed the almost linear $\delta R(\varepsilon)$ dependence and absence of the hysteresis under loading and unloading in combination with the high stability of a signal, detected for 2-hour testing at $\varepsilon \leq 10$ [9]. Such a tensoresistor, however, appeared highly sensitive to various gases, moisture, and working temperature; i.e., it should be protected against environmental factors.

The tensoresistors in the form of thin films, containing aligned single-walled CNTs (SWCNTs) on flexible substrates, exhibit the excellent elasticity ($\varepsilon \sim 280$ %), but the very low sensitivity ($S \leq 0.8$), high hysteresis, and insufficient strain measurement accuracy [10].

A MWCNT film placed between natural rubber layers showed the higher strain sensitivity (S ~ 43) at ε ~ 620 % [6]. However, the $\delta R(\varepsilon)$ dependence for this film is approximately linear only at $\varepsilon \leq 100$ %.

A new type of the tensoresistor, based on SWCNTs, encapsulated in the PDMS layers, was proposed in [11]. The parameters of $S \leq 6.3$ and $\varepsilon \leq 10$ % and the moisture resistance higher than that of the tensoresistor without a protective layer were reported. For the MWCNT film-based tensoresistor, the linear $\delta R(\varepsilon)$ portions were observed at $\varepsilon \leq 0.1$ % and $S \leq 0.35$ [12]. A similar tensoresistor, based on grapheme, encapsulated between the PDMS films, showed the high sensitivity (S ~ 30), but the low ($\leq$ 1 %) ε value [13]. Such a tensoresistor can apparently be used for fragile (rigid) objects, but not in medicine, where the high strain ($\varepsilon \geq 10$ %) is needed.

The parameters suitable for monitoring the strain of human organs were obtained in different CNT/PDMS tensoresistor structures [14, 15]. However, these devices demonstrate the high nonlinear responses and hysteresis in combination with the insufficient elasticity. For these structures, we have E ~ 0.4 – 3.5 MPa [16 − 18], whereas epidermal applications require the materials with E ~ 25 – 220 kPa [2]). The modulus of elasticity of PDMS increases after adding CNTs; therefore, the discrepancy between elasticity values for human skin and the tensoresistor grows. In addition, absorption of water (moisture) by PDMS leads to the enhancing rigidity and aging. The material becomes fragile and its E value significantly increases over the modulus of elasticity of human skin. Indeed, to exactly detect human skin movements, it is necessary to use high-efficiency strain gauges, containing more elastic (soft) materials than PDMS. Many drawbacks of the tensoresistor, based on the CNT-containing film, encapsulated in the PDMS layers, were eliminated using the modified PDMS (the so-called Ecoflex silicone rubber). The CNT/Ecoflex PDMS tensoresistor is characterized by ε ~ 500 %, broad $\delta R(\varepsilon)$ linearity portions, and negligible hysteresis (ε < 150 %), as well as high stability and repeatability of a detected signal during multiple (~2000) loading/unloading cycles [19].

Both in the CNT/PDMS and CNT/Ecoflex PDMS structures, PDMS is polymerized by heat treatment at a temperature of 70 °C for 2 h. Certainly, this procedure complicates fabrication of the devices.

The thin (< 100 nm) SWCNT-containing films on flexible polyethylene naphthalate substrates exhibited the optical transparency and resistance variation with the bending angle θ [20]. The bending sensitivity $S_\theta = \delta R/\delta\theta$ was found to be ~0.08 %/deg at $\theta = \pm 180°$. Here, θ is the bending angle and $\delta\theta$ is the θ increment; at $\theta = 0$, there was no film bending.

The composite nanomaterials, containing CNTs, deserve high attention. For example, the films, consisting of polimethyl methacrylate (PMMA) matrix, filled with MWCNTs, exhibited a linear strain of $\varepsilon \leq 1$% at 0.75 wt.% of MWCNTs [21]. In [22], a 80-μm-thick buckypaper was fabricated from thermoplastic polyurethane (TPU) and MWCNTs and the value of $\varepsilon \approx 180$% at a ratio of 80:20 between TPU and CNTs was attained. The tensoresistor, however, had a very narrow region of the linear strain dependence of the output signal ($\varepsilon \leq 1$ %) and the low strain sensitivity ($S \leq 2$).

Study of many nanocomposites, included in epoxy polymers and CNTs, showed that with an increase in the MWCNT concentration between 1−10 mass.%, the conductivity σ increases from 10^{-2} to 10^{2} S/m and the S value decreases from ~22 to ~3 [23 − 25].

The layers, consisting of the carboxymethyl cellulose (CMC) matrix, filled with ~5 wt. % of MWCNTs, demonstrate the high conductivity ($\sigma \sim 10^4$ S/m), $\alpha \leq 10^{-5}$ K^{-1}, and S ~ 10 [26, 27]. Laser techniques and nanotechnologies make it possible to control the characteristics of a tensoresistor in wide ranges; in particular, the main parameter, i.e., conductivity, can be changed within $\sigma \sim 10^{-1} - 10^4$ S/m. The degradation testing of the

CMC/MWCNT layers showed no significant σ variations upon multiple bending of flexible substrates. In particular, upon layer bending by θ = ±180° with a bending radius of 1 mm for up to 10 cycles, the conductivity hysteresis was no larger than 20% relative to its initial value. The hysteresis decreased with increasing number of measurement cycles and was no larger than 8% after 300 cycles. The high strain sensitivity (S_θ ~ 0.80 %/grad) was demonstrated on the CMC/MWCNT nanocomposite layers with thicknesses of 0.2 – 10 μm. This is higher than the parameter of S_θ ~ 0.08 %/grad reported in [20]. The layers did not exfoliate from substrates upon multiple bending, did not crack, and kept their initial exterior.

Various strain gauges, containing CNTs, were reviewed in [28 − 31]. Their operation is based on the measurements of resistance or capacitance of strained layers. In the first case, these are tensoresistors and the presented examples can be added with our group-II sensors. In the second case, the gauges are capacitive and usually consist of three layers; the flexible layer is placed between two MWCNT layers. Despite the acceptable parameters (S_θ ~ 0.2 %/grad and ε ≤ 100 %), the repeatability of the characteristics is complicated.

Above we described some tensoresistors that are promising for medical applications. Of special importance is their use as miniature epidermic strain or pressure gauges for controlling the recovery after complex surgery and tactile sense recovery. The authors of [32] carried out investigations in this direction: they formed miniature skin pressure gauge prototypes using a 3D printer [32]. However, the direct contact of the strain gauge with the human skin surface is allowed only at the high biocompatibility. Certainly, this approach is valid for the above-mentioned tensoresistors, including those based on CNTs.

Since CNTs and CNT-based nanocomposites are relatively new materials, the health and ecology risks have been thoroughly investigated. Numerous experiments with CNTs revealed both positive and negative effects. The positive effects of CNTs are the possibility of vector drug delivery to different (including brain) organism parts [33 − 36] and neuron and neurite growth assistance [37, 38]. The negative effects are acceleration of the destruction of duplex DNA fragments [39] and blood thrombocyte aggregation [40].

By now, the following aspects, concerning CNTs, have been established [41 − 45]: (i) pure CNTs are more dangerous than functionalized ones; (ii) the CNT toxicity significantly weakens in a composite nanomaterial; (iii) the CNT toxicity is lower than the toxicity of asbestos particles; (iv) in a biological medium, oxidative fermentation and biodegradation of CNTs occur; and (v) citrullination in cells can be indicative of cytotoxicity of CNTs at the early diagnostic stages [46]. The bovine serum albumin molecules are adsorbed and uniformly cover the SWCNT surface layer by layer; bovine fibrinogen molecules behave similarly. Thus, the modified SWCNTs appear almost nontoxical [47 − 49].

4. Conclusions

The overwhelming majority of diagnostic and therapeutic devices and systems require various sensors, including strain gauges. In particular, they are used to control the recovery after surgical operations or test thigmesthesia. In this work, we discussed some types of the layers with the tensoresistive properties and possibility of designing original medical tensoresistors on their base. The analyzed materials were divided into two groups: without CNTs (group I) and with them (group II).

- The group-I device, the most promising for medical applications, is an original tensoresistor, which represents a silicone elastomer, containing microchannels, filled with a conductive liquid [7]. Such a tensoresistor detects small bendings (θ < 120°) of human body parts with an error of 8%.

- The group-II tensoresistors, which are based on thin films, containing aligned SWCNTs on flexible substrates, exhibit the excellent elasticity (ε ~ 280 %), but very low strain sensitivity ($S \leq 0.8$), high hysteresis, and low strain measurement accuracy [10]. The

MWCNT film, placed between the natural rubber layers, demonstrated the highest strain sensitivity (S ~ 43) at ε ~ 620 % [6]. However, their $\delta R(\varepsilon)$ dependences are approximately linear only at $\varepsilon \leq 100$ %.

- In many cases, the CNT films were encapsulated between flexible PDMS layers. The tensoresistors of this type exhibit the highest parameters, including the maximum strain of ε ~ 500 % and the approximately linear dependence of the relative resistance variation on ε in the range of ε < 150%, as well as the stability and repeatability of the detected signal upon multiple loading/unloading cycles (~ 2000) [19].

Nevertheless, the above-mentioned gauges cannot be directly laminated onto a complex curvilinear human skin surface to control the skin surface dynamics with high accuracy. This limitation is related to the fact that the PDMS polymerization requires heat treatment at temperature of 70 °C for 2 h.

- In epoxy nanocomposites, the high strain sensitivity (~22) is implemented at the low MWCNT concentration (~1 wt.%) [23 − 25].

- The layers based on a nanocomposite, consisting of CMC and MWCNTs, showed the quite acceptable parameters, i.e., the high electrical conductivity (10^{-1} – 10^{-4} S/m) and bending sensitivity of ~ 0.80 %/grad.

In most cases, the region of tensoresistor linearity should be broadened, which is a complex problem. To do this, it is necessary to take into account not only the substrate elasticity, but also transparency of tunnel contacts at the points of nanotube adjustment in the CNT-containing layers [50]. In some cases, the above-described tensoresistors have the characteristics suitable for applications in medicine. However, their safety at the lamination onto the human skin has still been investigated and the results of these investigations are of crucial importance [32]. In addition, it should be taken into account that the tensoresistors need to be protected from moisture, temperature, gases, and other effects during their operation.

Thus, the results obtained yield a promising outlook of fabrication of the tensoresistors containing carbon nanotubes or nanocomposites based on them.

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