Flexible All-organic Highly Tenzo-resistive bi Layer Films as Weightless Strain and Pressure Sensors for Medical Devices

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Abstract—**The article is addressed to the development of flexible lightweight strain and pressure sensors capable of monitoring blood pulsing, breathing, and body movements. The prototypes of body sensing devices equipped with sensors based on all-organic highly tenzo-resistive bi layer films are described. The electrical resistance of the flexible sensors linearly and reversibly depends on deformation resulted from body movements. Sensors electrical responses suffice to measure very small pressure changes as well as delicate elongations in a wide deformation range.**

Keywords- piezoresistive covering; flexible, biocompatible pressure and strain sensors; organic molecular metal

I. INTRODUCTION

The development of flexible, lightweight, conducting materials, whose electrical transport properties strongly respond to delicate strain, brings great opportunities in the field of strain, pressure or bending sensors for their applications in intelligent textiles, robotic interfaces and body sensing devices [1-3]. Recently, we reported ultra-sensitive tenzo-resistive bi layer (BL) films composed of a polycarbonate (PC) matrix surfaced with crystallites of organic molecular metal β-$(ET)_2I_3$, were ET=bis(ethylene-dithio)tetrathiafulvalene (Fig. 1) [4, 5]. These BL films show ability to sense the uniaxial deformations given by the minimum value of a 10^{-3} % of relative strain that is well below those of many conventional strain gages [4]. The processing characteristics of polycarbonate films, "self-metallized" with the highly tenzo-resistive β-$(ET)_2I_3$-based layer, make them potentially useful for electronic applications where conductivity, lightweight, large or small area coverage and flexibility are required [4]. Moreover, it has been shown that BL films can be successfully integrate in textiles [6]. The BL film-based strain gages can be engineered with gage factors (S) up to 20 and different temperature resistance coefficients [4, 5]. The tests have shown that BL film-based pressure sensors, being *biocompatible*, are able to control intraocular pressure changes [7]. The contact IOP sensing lens with a membrane pressure sensor based on the above mentioned BL film is already under development [7, 8].

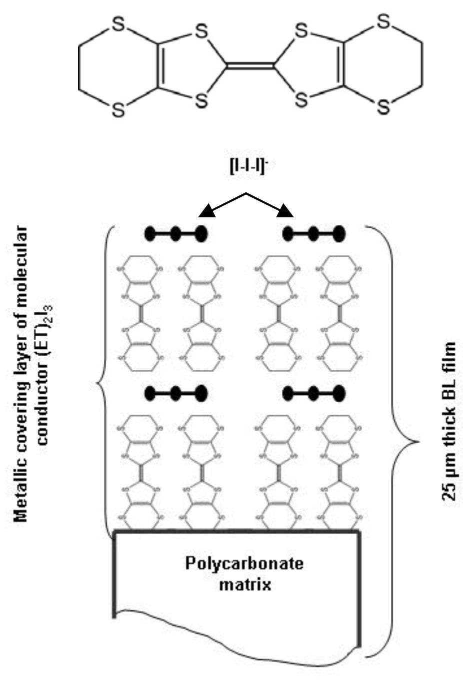

Figure 1. Top: Skeletal formula of bis(ethylenedithio)tetrathiafulvalene (ET); bottom: schematic view of the orientation of $(ET)^{+0.5}$ radical cations and $[I\text{-}I\text{-}I]^-$ anions in a metallic covering layer of β-$(ET)_2I_3$ formed at the surface of a polycarbonate film.

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In order that a tenso-resistive BL film can sense pressure changes, it should be located in devices as a membrane. In this case the electrical resistance of a BL film will respond to its bending deformation resulted from a pressure change. We used this engineering approach to fabricating the set of medical sensing prototypes.

Here we report a promising approach to engineering biocompatible and highly tenzo -resistive membranes for their applications to monitoring medical parameters. The prototypes of medical devices capable of controlling the body movements are presented

II. FABRICATING FLEXIBLE SENSING MEMBRANES

In line with the early reported method [9] we first prepared a 25 μm thick polycarbonate film spiced up with an 2 wt. % of ET that is a precursor for organic molecular metal $(ET)_2I_3$. The film was cast on a glass support at 130 ^oC from a 1,2-dichlorobenzene solution of PC and ET. In order to cover the film with a layer of $(ET)_2I_3$, we exposed the film surface to the vapors of a saturated solution of iodine in dichloromethane. The covering mechanism is following: the surface of a polycarbonate film easily swells under its exposure to dichloromethane vapors; this swelling facilitates a migration of ET molecules from the film bulk to the swollen film surface where the part of ET molecules are oxidized to radical cations $ET^{+\bullet}$ by iodine, which penetrates in the film surface together with dichloromethane vapors. This redox process induces the rapid nucleation of highly insoluble $[(ET)^0(ET)^{+\bullet}](I_3)^-$ species and a facing layer of molecular metal α-$(ET)_2I_3$ is formed. Electrical resistance of the 25 μm thick BL film with the covering layer of α-$(ET)_2I_3$ responded to strain with a gage factor being 10, whereas the polycarbonate film with the same thickness but surfaced with β-$(ET)_2I_3$ has a gage factor being 20 [4]. The BL film covered with a highly piezoresistive layer of β-$(ET)_2I_3$ was formed via a thermo-activated $\alpha \rightarrow \beta$ phase transition that occurs at T>100 ^oC [9]. For this purpose the BL film covered with the layer of α-$(ET)_2I_3$ was annealed at 150^{o}C during 30 min. The formation of the covering layer of β-$(ET)_2I_3$ was confirmed by its X-ray diffraction pattern that shows only one line at $2\theta=5.8^o$ and its higher order reflections, that corresponds to "c"-oriented crystallites of organic metal β-$(ET)_2I_3$ (Fig. 1, bottom) [9]. The surface analysis on a micro scale, performed using "Quanta FEI 200 FEG-ESEM" scanning electron microscope (SEM), showed that the crystallites of the covering layer of β-$(ET)_2I_3$ are of nano or submicro sizes (Fig. 2). The calculated possible maximal thickness of the piezoresistive covering layer is around 250 nm.

As a final remark to this part we would like to add that the BL film temperature resistance coefficient (TRC) and its gage factor were found as 0.3 %/^{o}C and 20, respectively. These values are in excellent agreement with the early reported data [4]. The TRC was calculated as a relative resistance change per grade and gage factor was calculated as the ratio between the relative resistance change and the relative strain value.

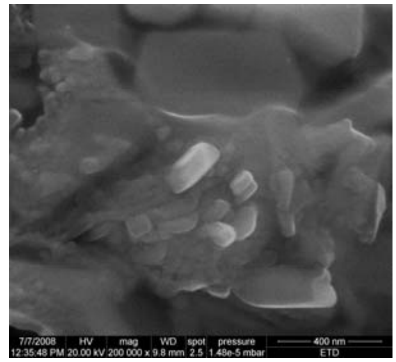

Figure 2. SEM image of the piezoresistive covering layer of β-$(ET)_2I_3$;

III. PROTOTYPES OF BODY SENSING DEVICES

The simple sensing prototype devices for monitoring the body movements breathing rhythms [4] blood pulse, intraocular pressure [7, 8] finger movement are already under development. Below we present some of them.

Blood pulse sensor (Fig. 3). The BL film-based membrane with sensing layer of β-$(ET)_2I_3$ was equipped with electrical contacts and fixed between two rigid plastic rings. To measure pulse the device was fixed on the carpus of a volunteer (Fig. 3 bottom). The resistance response of the sensor to strain provoked by pulse movement was measured by a four probes dc method. Data were gathered for different persons and time periods. As seen in the Fig. 4, the pulse movement resulted in an oscillated resistance curve that can be easily recorded and analyzed.

Figure 3. Photo images of the blood-pulse sensor (Top) and sensor location on the carpus of a volunteer under pulse testing (Bottom).

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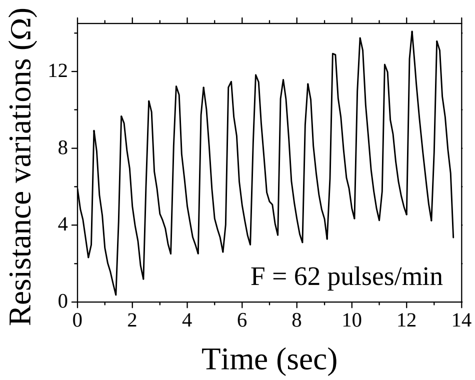

Figure 4. Resistance response to the blood-pulse movement.

Breathing sensor. This prototype contains the BL film as a tenzo-resistive diaphragm on springy plastic U-shape plate, which was attached to an elastic-textile belt (Fig. 5). The resistance response of sensors to strain provoked by the breathing was measured by a four probes dc method. Data were gathered for a different persons and time periods. As seen in the Fig. 6 the breathing movement resulted in an oscillated resistance curve that can be easily recorded and analysed. A relatively long time periods between the oscillations, observed in Fig. 6, correspond to holding up breathing.

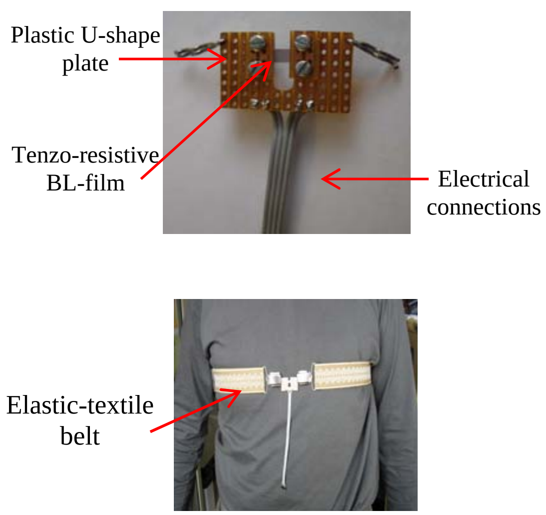

Figure 5. Photo images of the breathing sensor (Top) and sensor location on the breast of a volunteer for monitoring his breathing (Bottom).

Devices for monitoring finger movement. The first prototype of such type of medical devices is now under development. The prototype uses the BL-film as a tenzo-resistive diaphragm. The fabricated prototype is capable of measuring a very delicate finger movement as an easily controlled electrical signal. Its design also permits tracking of the large-scale finger movement.

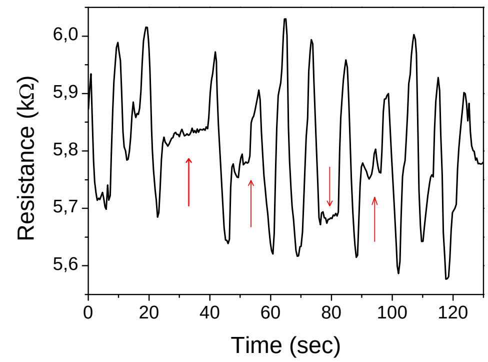

Figure 6. *Resistance response to the breathing of* a volunteer*; red arrows correspond to holding up breathing.*

IV. Summary

It was shown that electrical resistance of flexible sensors with the active layer of tenzo-resistive organic metal $(ET)_2I_3$ linearly and reversibly depends on deformation resulted from the body movements.

The preliminary data display that the polycarbonate films metallized with β-$(ET)_2I_3$ show considerable promise as flexible strain/pressure gages for use in detecting body movements. Therefore this type of lightweight sensors is able to take the place of conventional metal-based strain and pressure gages in monitoring biomedical high-tech.

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References

[1] S. Y. Yurish, N. V. Kirinaki, and I. L. Myshkin, "World Sensors and MEMS Markets: Analysis and Trends", Sensors & Traducers Magazine (S&T e-Digest), vol. 62, Issue 12, pp. 456-461, 2005.

[2] F. Axisa, P. M. Schmitt, C. Gehin, G. Delhomme, E. McAdams and A. Dittmar, "Flexible technologies and smart clothing for citizen medicine, home healthcare and disease prevention", IEEE Transactions on Information Technology in Biomedicine, vol. 9, No. 3, pp. 325-336, 2005.

[3] B. Adhikari, S. Majumdar, "Polymers in sensor applications", Progress in Polymer Science, vol. 29, pp. 699-766, 2004.

[4] E. Laukhina, R. Pfattner, L. R. Ferreras, S. Galli, M. Mas-Torrent, N. Masciocchi, V. Laukhin, C. Rovira, and J. Veciana, "Ultrasensitive Piezoresistive All-Organic Flexible Thin films", Adv. Mater., vol. 22, pp. 977-991, 2010.

[5] E. Laukhina, R. Pfattner, M. Mas-Torrent, C. Rovira, J. Veciana, Vladimir Laukhin, "Film-based Sensors with

Piezoresistive Molecular Conductors as Active Components: Strain Damage and Thermal Regeneration", Sensors & Transducers Journal, , vol. 10, Special Issue, February, pp. 1-12, 2011.

[6] L. R. Ferreras, R. Pfattner, M. Mas-Torrent, E. Laukhina, L. López, V. Laukhin, C. Rovira, J. Veciana *J.* "Highly piezoresistive textiles based on a soft conducting charge transfer salt", Mater. Chem**.**, vol. 21, pp. 637- 641, 2011.

[7] V. Laukhin, I. Sánchez, A. Moya, E. Laukhina, R. Martin, F. Ussa, C. Rovira, A. Guimera, R. Villa, J. Aguiló, J.-C. Pastor, J. Veciana, "Prototype for Noninvasive IOP Monitoring with a Nanostructured Polymeric Sensor Embeded in a Contact Lens", Transducers & Sensors, 2010, to be published.

[8] V. Laukhin, C. Rovira, E. Laukhina, J. Veciana, M. Mas-Torrent, A. Quimera Brunet, J. Aguiló Llobet, R. Villa Sanz, J. C. Pastor, and F. Ussa, Truncated contact lens for use in telemetry system, has truncation plane provided parallel to base of lens, and centrally placed polymer nanocomposite material joined to perimeter of truncated zone, Patent: ES2330405-A1; WO2009147277-A1.

[9] E. E. Laukhina, V. A. Merzhanov, S. I. Pesotskii, A. G. Khomenko, E. B. Yagubskii, J. Ulanski, M. Krysezewski, J. and K. Jeszke, "Superconductivity in reticulate doped polycarbonate films containing $(BEDT\text{-}TTF)_2I_3$", Synth. Met., vol 70, pp. 797-800, 1995.