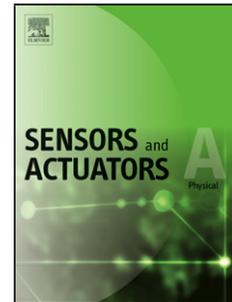# Accepted Manuscript

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Thermal sensor based on a polymer nanofilm

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Abstract

In this work, we have developed a thermal sensor based on poly(3,4 ethylenedioxythiophene) (PEDOT) nanofilms as thermoelectric material. The PEDOT nanofilms have been synthesized by the electrochemical polymerization method. The thicknesses of the films were around 120 nm. The doping level of PEDOT was controlled by chemical reduction using hydrazine. The achieved Seebeck coefficient is 40 μV/K. A PEDOT nanofilm was integrated into an electronic circuit that amplifies the voltage originated from the Seebeck effect. The temperature increment produced by a fingerprint touching the film is enough to switch on a light emitting diode.

Keywords: thin films, thermoelectric, conductive polymers, thermal sensors

1. Introduction

The number of researches investigating organic materials for electronic applications has been remarkably incremented during the last years [1, 2, 3]. Especially, energy applications have become in the focus of a large number of studies related to organic materials [4, 5, 2, 6, 7, 8]. Focusing on their repercussions on nowadays society, it can be highlighted the use of these materials in solar cells [8, 9], supercapacitors [2, 6, 7] and thermoelectric devices [4, 5, 10]. The use of organic materials such as conductive polymers entails numerous advantages over traditional inorganic semiconductors. The most important advantages are: low cost and abundance of raw materials, absence of toxicity, good mechanical properties, and easy chemical modification. Furthermore, conductive polymers can be easily nanostructured by different methods [11, 12], thus showing better performance than their bulk counterparts since phonon scattering and energy-dependent scattering of electrical carriers decrease in the presence of nanoscale interfaces [13, 14, 15].

The use of conductive polymers for thermoelectric applications has been outstandingly increasing during the last 5 years. Proof of this is the increasing number of publications on thermoelectricity including conductive polymers. The thermoelectric efficiency can be measured by the parameter ZT ($ZT = \sigma S^2 T/\kappa$, where σ is the electrical conductivity, S the Seebeck coefficient, T the temperature, and κ the thermal conductivity, with an electronic and phononic contributions), the dimensionless figure of merit. ZT values around 0.2-0.4 have been attained for poly(3,4 ethylene-dioxythiophene) doped with several courter-ions such as: polystyrene sulfonate (PSS) [16], p-toluene sulfonate (Tos) [17], perchlorate or bis(trifluoromethylsulfonyl)imide (BTFMSI) [5]. Currently, PEDOT is considered one of the most promising organic thermoelectric materials and could be a good competitor to classical inorganic thermoelectrics such as Bi_2Te_3. The main problem of the organic semiconductors at this point is its low efficiency, restricting its use in power generator applications. However, it can be used as a thermal sensor due to its good thermoelectric response.

Figure 1: Scheme of the electronic circuit of the thermal sensor and the load

The sensor based on thermoelectric materials use the Seebeck effect to detect changes in the temperature. Conductive polymers can offer numerous advantages for sensor applications, due to their good mechanical properties such as flexibility, and easy nanostructuration. This fact is very important to miniaturize electronic circuits used as nanosensors. In this work, we have developed a thermal sensor based on a PEDOT nanofilm attached to an electronic circuit able to switch on a light emitting diode with temperature changes around room temperature. We have simulated the behavior of the sensor using a 3D finite element model with the aid of COMSOL Multiphysics.

2. Experimental

2.1. Materials

The reactants used in this study were: 3,4-ethylenedioxythiophene, 1-butyl-3-methylimidazolium hexafluorophosphate, and acetonitrile, purchased from Sigma Aldrich Co.

2.2. Synthesis of PEDOT nanofilms

The PEDOT films have been obtained by the electrochemical polymerization method on a gold thin film (20 nm), previously deposited on a PET substrate by metal evaporation in a Univex 300 Evaporation system. The synthesis was carried out in an Ivium-n-Stat: a multi-channel electro-chemical workstation under computer control with a Pt grid as a counter electrode, a PET gold covered substrate as the working electrode and a Ag/AgCl electrode as the reference one. The PEDOT was polymerized from a 0.01 M solution of EDOT and 1-butyl-3-methylimidazolium hexafluorophosphate 0.01 M in 100 ml of acetonitrile at 3 mA during 1.5 minutes. Under these experimental conditions, the PEDOT film thickness was 110-120 nm. The gold layer of the working electrode was removed after the PEDOT synthesis with an acid solution (HNO_3:HCl ratio 1:3). The PEDOT nanofilms were rinsed several times with water and ethanol to remove the untreated monomer and then dried in air at room temperature. Finally, the samples were reduced in a hydrazine (N_2H_4) vapor atmosphere during 25 seconds.

2.3. Sensor fabrications

Figure 1 shows the scheme of the electronic elements which forms the thermal sensor. This device is composed by: i) a PEDOT nanofilm attached to two blocks at different temperatures (T and T_0), ii) a circuit amplifier with a high differential gain (Gd), of about 100 dB, iii) a light emitting diode connected at the output through a load resistance and v) a power supply with an electromotive force (emf) of $\pm5V$. The electronic circuit is composed by an ANI 129 (or an AD620AN) OP amplifier, two OP amplifiers (OP177GP) as a voltage reference and the final fit of the gain in differential mode was performed through a non reversible structure. The negative emf is actually not necessary here for this application (since the temperature difference will be always positive), VEE can be connected to ground.

2.4. Characterization

The Seebeck coefficient is determined as the ratio between the electrical potential, ΔV, and the temperature difference, ΔT, that is:

$$S = \frac{\Delta V}{\Delta T} \quad . \tag{1}$$

The Seebeck coefficient was determined using a home made apparatus. It was built with two copper blocks kept at different temperatures ($T > T_0$) connected with the PEDOT film as shown in Figure 1a. The hot and cold blocks, at T and T_0 respectively, are controlled by a Lakeshore 340 temperature controller by means of two PT100 resistors as temperature sensors. The cold end at T_0 is cooled by a water stream coming from an inertial bath. A Keithley 2750 switching system controlled by a Labview program was used to monitor the potential data.

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3. Results and discussion

Among the substrates that can be used to obtain PEDOT by electrochemical polymerization, in this paper we have chosen PET since it is a polymer with good flexural properties. The flexibility was kept after the PEDOT layer was synthetized over the PET substrate. The polymerization time and intensity during the electrodeposition process determine the thickness of the film. Previous experiments [5] correlated time and intensity with the thickness of the PEDOT films. In this paper, we have chosen 3 mA and 1.5 min to obtain a 120 nm thick PEDOT film as shown in **Figure 2a**.

Figure 2: (a) Image of PEDOT nanofilm; (b) Schematic diagram of the Seebeck measurements. (c) Seebeck voltage as a function of temperature difference across the sample.

The measurements of Seebeck coefficient were made with a homemade apparatus as shown in Figure 2b. The sample (see Figure 2a) was attached between two copper blocks to guarantee a good thermal conductivity. One of these blocks was kept at room temperature (T_0) while the other one is heated to different temperatures, T being $T > T_0$. Figure 2c shows the output or Seebeck voltage as a function of temperature difference created across the polymer nanofilm. The sample was subjected to a reduction process using hydrazine vapor to increase the Seebeeck coefficient of the sample. As shown in Figure 2c, the Sebeeck coefficient changes from 9 μV/K to 40.1 μV/K by reducing the PEDOT. This fact is related with the doping level of the sample; since the hydrazine is a reduction agent, the oxidation level of the PEDOT chains decreases [5]. Due to this process, the polymer chains change from a polaronic/bipolaronic state for the pristine sample to a neutral state for the reduced one, as have been previously reported [18, 19]. The increase of the Seebeck coefficient improves the sensitivity of the thermal sensor.

Figure 3: Temperature mapping of a polymer thin film simulated with COMSOL software.

The electric behavior of the thermal polymer sensor (Figure 2b) has been simulated with a COMSOL Multiphysics Modeling Software. The following parameters have been used for the simulation: 0.2 W/m K for the thermal conductivity, 200 S/cm for the electrical conductivity and 40.1 μV/K for the Seebeck coefficient. The sample dimensions were 20×5 mm^2 and the thickness was 1 μm. Figure 3 shows the temperature mapping simulation of the polymer thin film. The film is connected to a variable load resistance in order to check the optimum impedance for the maximum energy transfer.

Figure 4: Simulation of power generation as a function of current intensity for the polymer thermal sensor at several temperature differences.

In addition, power simulations generated by different temperature increments between the two blocks as a function of the current intensity have been obtained with the COMSOL software. Figure 4 shows the power generation simulations as a function of the electric current across the sample for several temperature differences. The dependence between power and current is of parabolic type. As the temperature difference increases, the maximum value of the power is shifted to higher values when the current increases. This fact is explained by an increase of the voltage across the sample produced by the Seebeck effect.

In order to check experimentally the data previously simulated, the PEDOT nanofilm (Figure 2a) has been successively pressed by a finger and the output signal has been recorded. Figure 5 shows the temperature difference and the output or Seebeck voltage generated when the PEDOT nanofilm is pressed by a finger. These results indicate that the finger creates a temperature difference of around 1.5 K (Figure 5a) on the film. The temperature gradient results show a good correlation between the data calculated from the Seebeck voltage and that measured from the PT100 resistors. The reproducible voltage of 60-65 μV is recorded with a very good time response of 0.52 s.

A device on-off type that uses a PEDOT film as thermal sensor (Figure 6a) has been developed. The high CMRR (above 100 dB) of the electronic circuit in conjunction with its large differential gain (larger than 90 dB) makes it possible to use a very small input voltage (Figure 6a). For this reason, the voltage generated by the finger pressing the PEDOT film, 200 μV, with a temperature difference of about 5 degrees can be used for the device operation. The noise can be neglected because the common-mode gain (Gc) is almost zero. The output of the operational amplifier is

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Figure 5: (a) Temperature increment, and (b) voltage output generated by finger pressing the thermal polymer sensor.

Figure 6: (a) Picture of the sensor device. (b) Input and output voltage during several finger pulses.

saturated with a very low differential pressure (in the order of $80\mu V$). When a finger pulse ($\Delta T \approx 5°C$) is applied, the output voltage (Figure 6b) is enough to switch on an LED as shown the Figure 6a.

4. Conclusions

We have developed a thermal sensor based on the thermoelectric effect acting on a polymeric materials. A PEDOT nanofilm has been obtained from electrochemical polymerization from EDOT monomers on a PET substrate covered with gold. The PEDOT nanofilm has been used as thermal sensor based on the Seebeck effect. A simulation using COMSOL Multiphysics indicates the temperature and voltages differences that can be generated. An electronic device that uses the voltage generated by the temperature difference due to a finger pressing the polymer has been constructed. The device can switch on an LED.

Acknowledgements

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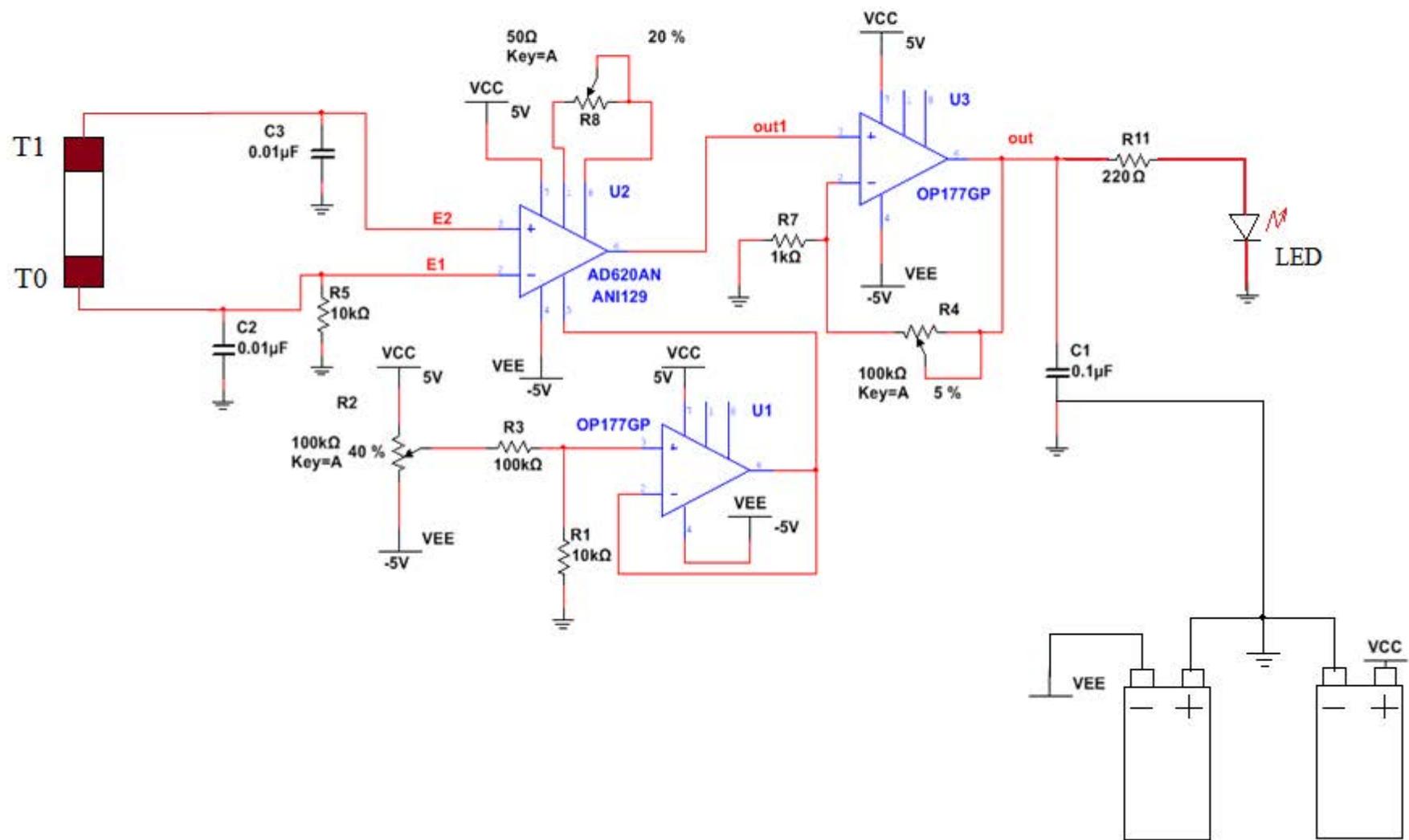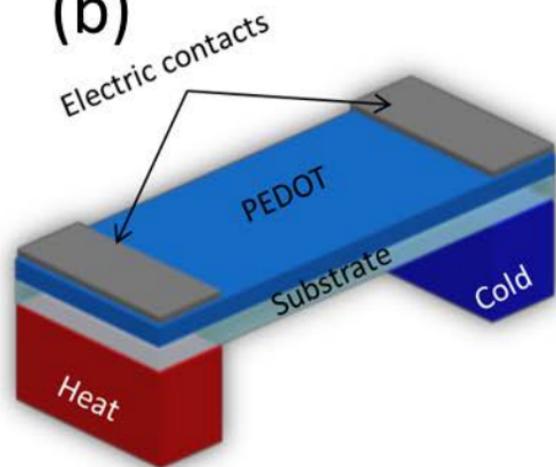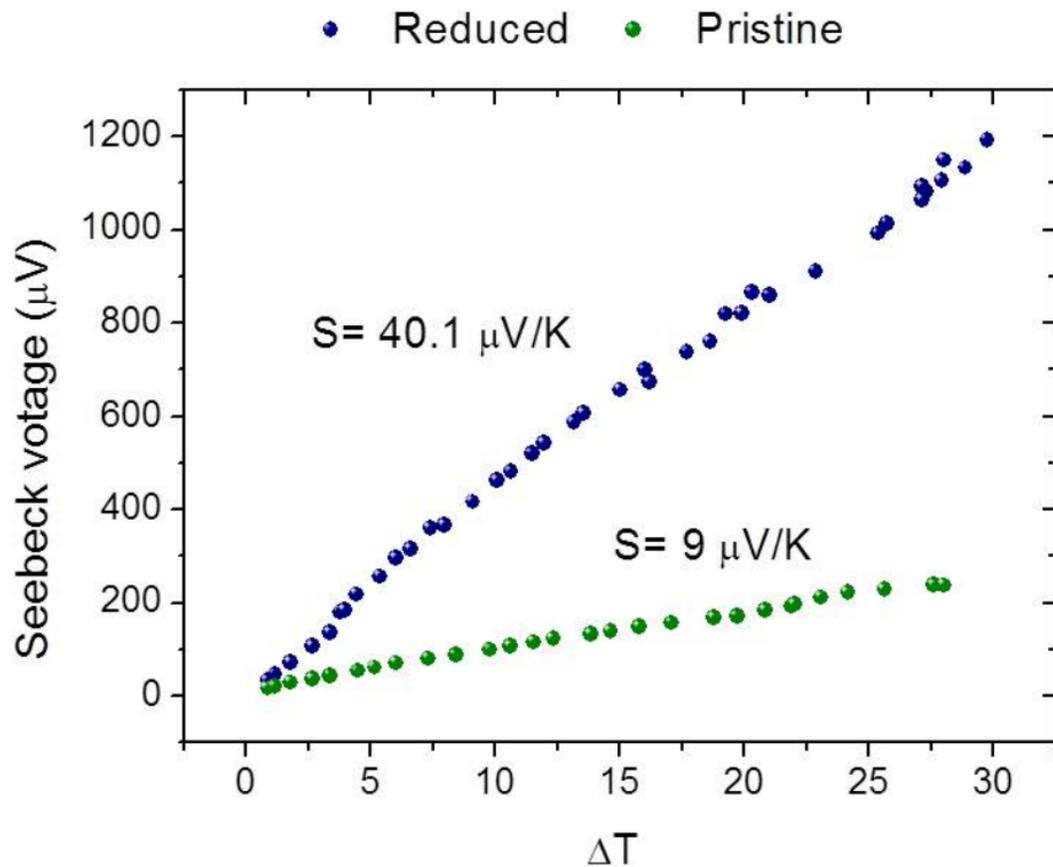
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Figure(if any)

Figure(if any)

(a)

(b)

Electric contacts

PEDOT

Substrate

Heat

Cold

(c)

Reduced   Pristine

S= 40.1 μV/K

S= 9 μV/K

Seebeck votage (μV)

ΔT

Figure(if any)

(a)

(b)

INPUT (FINGER PULSE)

OUTPUT (ON/OFF LED APPLICATION)
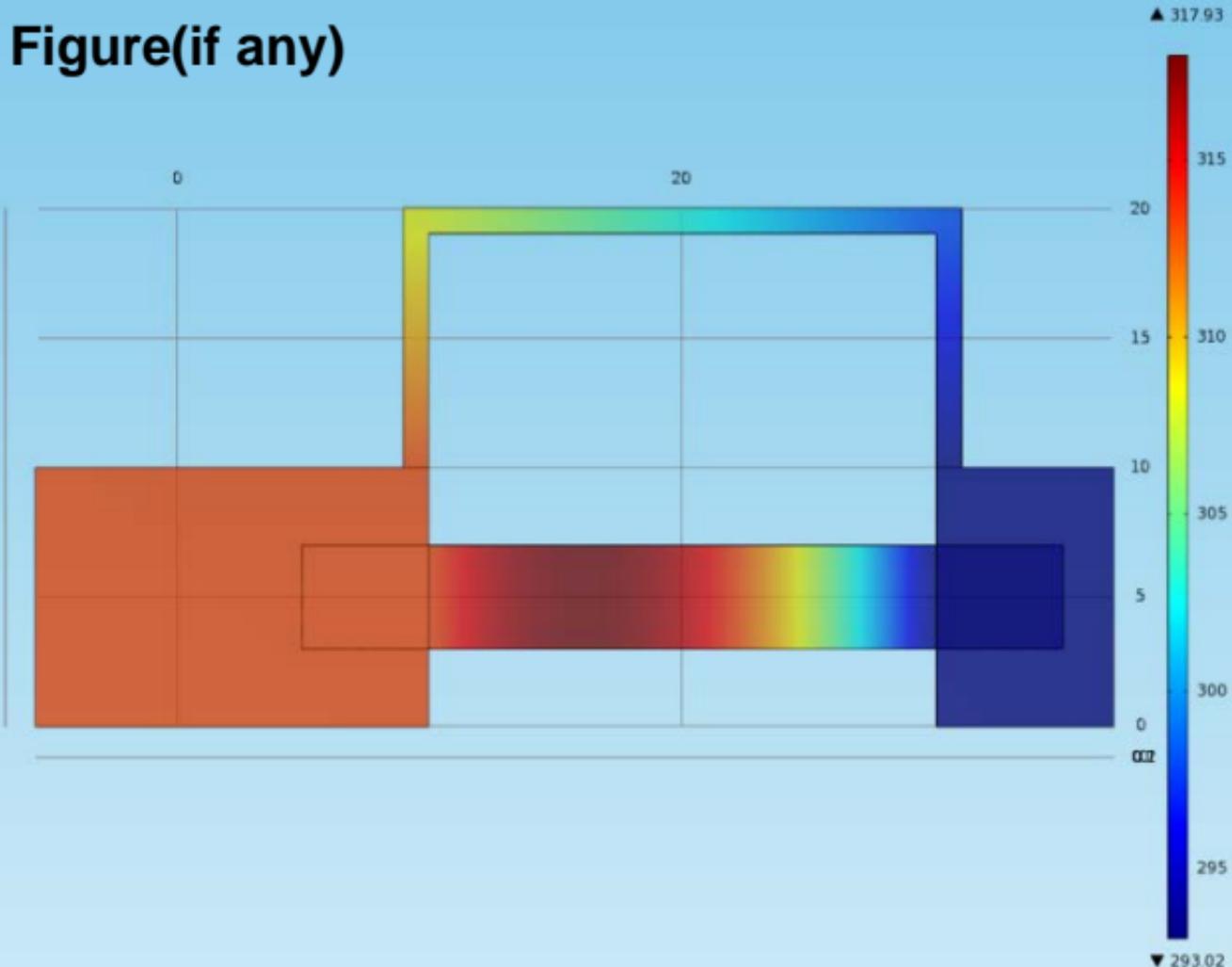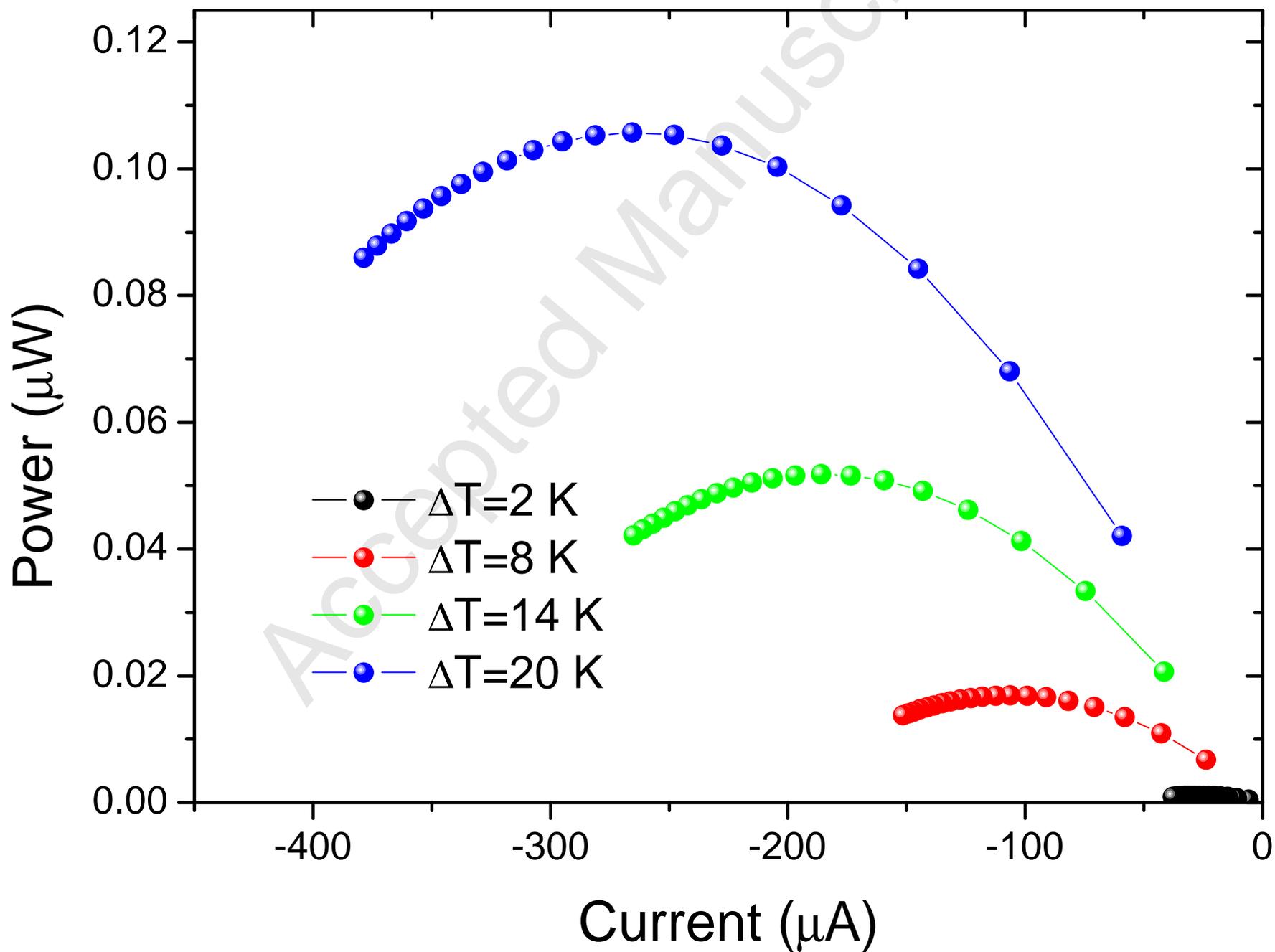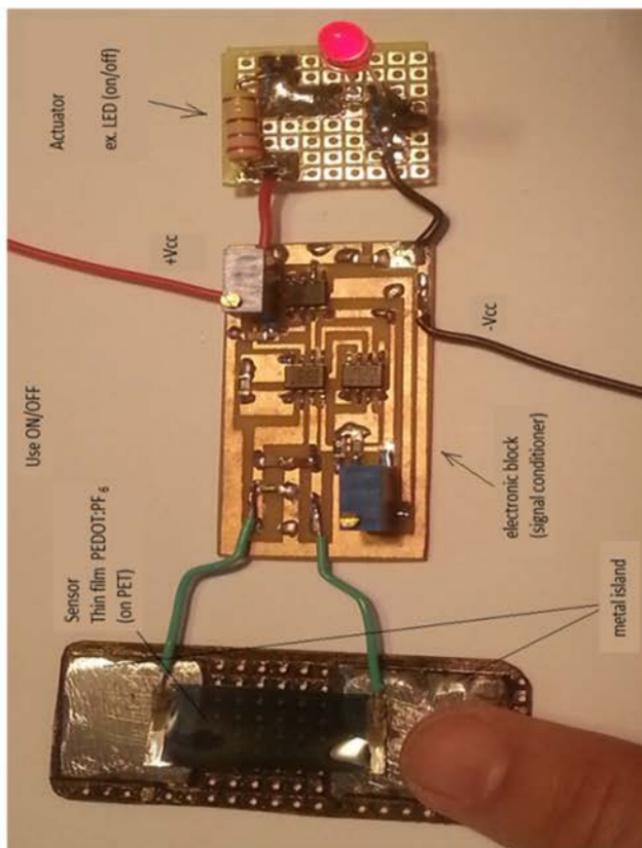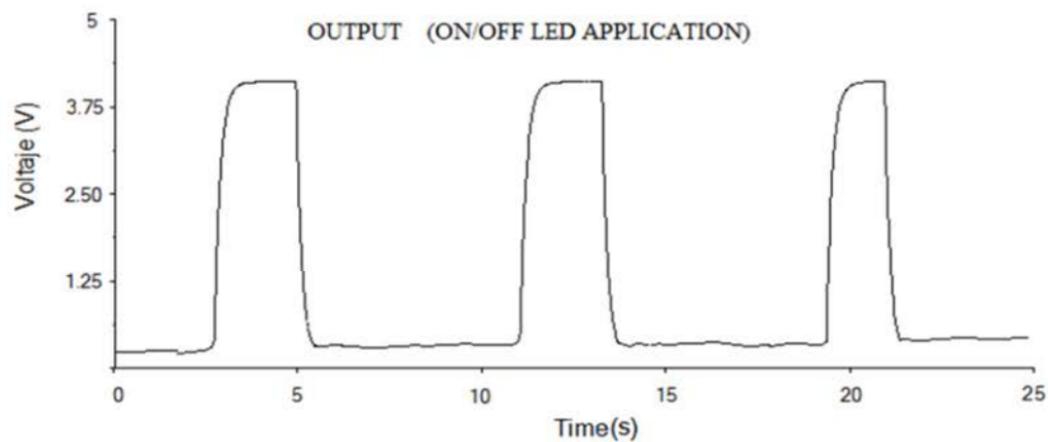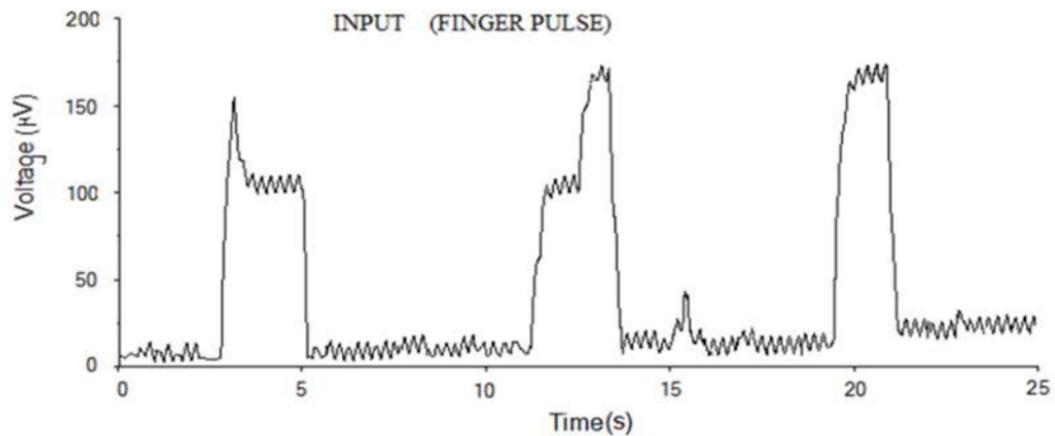
Highlights

- The PEDOT nanofilm has been used as thermal sensor based on the Seebeck effect.
- An electronic device that uses the voltage generated by the temperature difference due to a finger pressing the polymer has been constructed.
- The device can switch on an LED.

AUTHOR BIOGRAPHY

Mario Cuelebras obtained a Degree in chemical from the University of Valencia in 2011. After he obtained a Master in science and technology in colloids and interfaces. He started his phD studies In 2012 under direction of Andres Cantarero, about "Organic thermoelectric materials" in University of Valencia. Currently he has several papers published about thermoelectricity in polymeric and carbonaceous materials.

Antonio López received his Ph. D. degrees in Electronic Engineering from the Technical University of Catalonia (UPC), Barcelona, Spain, in 2005. Since 1990 he joined the Department of Electronic Engineering where he currently working as Associate Professor. He teaches courses in Microelectronics, Digital Electronic and Renewable Energy at different levels. Currently leads a research team on thermoelectricity.

Clara M Gómez studied Chemistry at the University of Valencia where she received her doctoral degree in 1990. She did her postdoctoral stage In Cranfield University working on the cure behavior of epoxy composites. At this moment she is Professor of Physical Chemistry at the University of Valencia. Her research work is being developed in The Institute of Materials Science. The main areas of research are thermodynamics of polymer blends, cure monitoring of thermoset polymers, new polymers for thermoelectric applications and polyurethane thermoplastics, including thermal, mechanical, electrical and spectroscopic characterization.

Andres Cantarero finished his PhD in Valencia in 1986. After his postdoc (Max Planck Institute, Stuttgart, Germany), he joined the University of Valencia, where he now is full professor. He has worked in semiconductor nanostructures, especially in Raman spectroscopy and photoluminecence techniques. He has developed phenomenological models on the electronic structure an lattice dynamics of semiconductors. He has also applied ab initio techniques for the calculation of the electronic structure and optical properties of material.