Electrospun Polymeric Fibers Coated With Pd As A Sensitive Layer For Hydrogen Detection

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Abstract — **Polymeric fibers can be used in several fields of research and technology depending on the type of polymer and the diameter of the fiber used. One of the most important features inherent to fibers is the large surface area that can be explored in applications like sensors. The electrospun fibers could be modified depositing metals by means of the electroless deposition technique in order to be used as sensitive layer. In this work is presented a gas sensor that has a sensitive layer made by polymeric fibers covered with palladium deposited by the electroless technique. The polymeric fibers were electrospun over a gold comb structure fabricated onto a silicon substrate with a distance between fingers of 50 µm. The fabricated sensors were reproducible with relative resistance response of 0.35% for H_2 concentration of 100ppm under a controlled temperature of 25°C, which means a sensor capable of measuring residual concentrations.**

Index Terms—electrospinning, nanofiber, electroless deposition, sensors, hydrogen.

I. INTRODUCTION

For environmental monitoring, nowadays exist an increasing interest to detect hydrogen and hydrocarbons that can be found in marine and atmospheric environments, and in the process of oil production. Chemical sensors can be used for gas detection of gas leaks in clean rooms, leak detection in gas compressors, fail monitoring of high-voltage transformers and ripening process of fruits [1-6].

In the last decade the electrospinning process became an important process to obtain polymeric fibers because it offers an easy and low cost way to obtain micro and nanometric fibers. [7,8]. Also, polymeric fibers can be applied in several important fields, of research and technology, depending on the type of polymer or blend of polymers used as precursor solution. Moreover, depending on the application we can have a single fiber or an electrospun fiber mat. In both cases the diameter and morphology of the fiber play an important role. [9, 10]. One of the most important features inherent to the electrospun fibers is the large surface area that can be explored in applications like filtration, preconcentration and sensors [9, 11, 12, 13].

To achieve these applications, the fibers may be modified in different ways; e.g. particles can be incorporated into the precursor solution in order to add their own properties to those of the polymer [9, 14,15]. Another way is to deposit layers of metal by electroless deposition technique which has the advantage of being non-destructive and enables fibers uniformly coated with metals. Unlike conventional metal evaporation, electroless deposition covers selectively the entire fiber with the metal without any shadow effect [9, 16-21]. The resulting fibers, coated with metal, are useful for use in gas sensors that are based on varying electrical resistance. Thus, it is possible to associate the large area to volume ratio offered by the fibers with the sensing properties of metals to fabricate sensors for different chemical species including NH_3, H_2S, NO_2, CO, H_2O amines, alcohols, and volatile organic compounds (VOCs).

Palladium has been employed as a sensitive layer to detect hydrogen using the change of their conductive properties as a chemioresistor fabricated as thin layers or in the nanofiber matrices [2, 5, 22]. It has several advantages including a high permeation coefficient [22], ease of adsorption [2, 5], workfunction control of the Pd/oxide interface [22], optical and conductive properties changed by the hydrogen content [22]. In addition, literature presents very few applications using nanofibers with palladium incorporated into their matrices although they may have a great sensitivity as chemioresistors due to their large areas [2]. The work of Nikfarjam et al. [2] is one of the few articles of electrospun Pd-doped WO_3 nanofibers used as chemioresistors.

On the other hand, Lundstrom et al [22, 23] modeled the hydrogen diffusion in the Pd layers. Nowadays, it is well known that the hydrogen molecule break at the palladium surface and the hydrogen atoms adsorbs on it. The hydrogen loses an electron to the Pd and the ion H^+ diffuses through the metal layer. The ion H^+ recovers the electron and concentrates on the Pd/substrate interface. In addition, for temperatures around 100°C, the phase PdH is formed, which changes the optical properties [22]. Based on the Lundstrom´s model, the electrical resistance of the Pd layers can change with the environmental hydrogen concentration (C_{H2}) as follows [22, 23]:

$$\frac{\Delta R}{R} = \frac{\Delta R_{MAX}}{R}\left(\frac{k(T)\sqrt{C_{H2}}}{1+k(T)\sqrt{C_{H2}}}\right) \quad (1)$$

where C_{H2} is the hydrogen concentration over the Pd film and *k(T)* is a constant dependent on the temperature and on the adsorption characteristics of the hydrogen onto Pd.

Aiming at combining the facility for fabrication of polymeric fibers by electrospinning with the advantages of the electroless deposition technique, in this work, it is presented for the first time a gas sensor that has a sensitive layer based on polymeric fibers covered with palladium deposited by electroless technique. It will be shown that the combination of the larger area offered by the mat of nanofibers with the properties of palladium in this structure allows to fabricate reproducible sensors capable of measuring residual concentrations of hydrogen higher than about a hundred of ppm.

II. EXPERIMENTAL

Fig. 1 shows the gold comb structure used. It was fabricated over a high resistive silicon substrate, which has two external pad contacts with a distance between fingers of 50 µm. The structure was mounted over an alumina substrate and a thin copper wire was glued into the pads using carbon paste, in order to allow the connection with the measurement instruments.

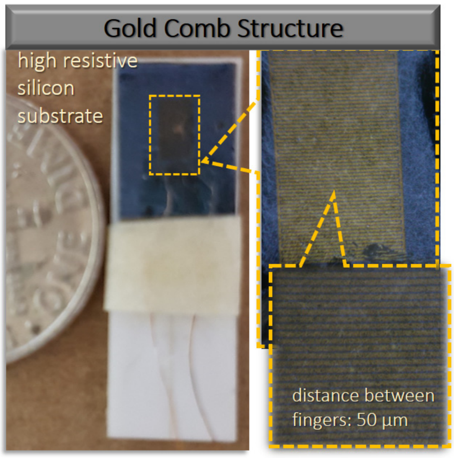

Fig. 1 - Gold comb structure over the alumina substrate. Details show the fibers over the structure.

The sensitive layer consists of a mat of polymeric fibers coated with palladium deposited by electroless process. This layer was electrospun over the gold comb structure as illustrated in Fig. 2.

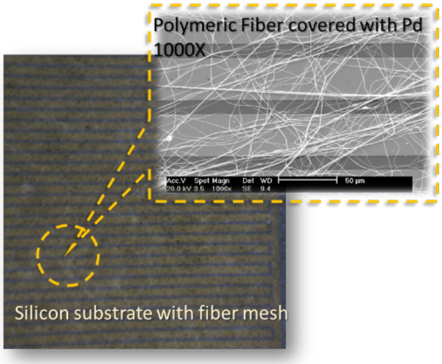

Fig. 2 - Gold comb structure with the electrospun polymeric fibers over it.

The polymeric fibers were produced by electrospinning process using a homemade apparatus consisting of a DC high voltage source (Gamma High Voltage Inc. 0-30 kV), as a "reactor" a plastic syringe with a hypodermic needle (21G 1") and a grounded metallic collector were the fibers are collected. The apparatus is depicted in Fig. 3.

The 8% w/w precursor solution was prepared dissolving Polyacrylonitrile (PAN) in N, N-Dimethylformamide (DMF), both from Sigma Aldrich, and stirred until the complete polymer dissolution. The solution was loaded into the syringe and kept 20 cm from the sample. The positive terminal of the DC high voltage power supply was connected to the needle and the ground terminal was connected to metallic collector where the sample is placed. The fibers were electrospun over the interdigitated structure, which was previously defined on the silicon substrate as illustrated in Fig.1.

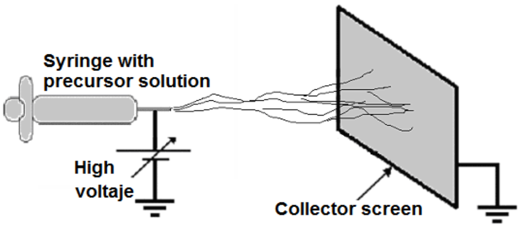

Fig. 3 - Electrospinning apparatus

The electroless deposition process was used in order to recover the entire surface of the fiber with a uniform Pd layer. The recipe of the selective deposition of palladium on the surface of the polymeric fibers is composed of the following steps:

1) Surface activation with a stannous solution:
Immersion in 0.1 g/L $SnCl_2$ solution for 5 min.
2) Surface deposition of Pd sites by Sn displacement:
Immersion in 0.1 g/L of $PdCl_2$ and 50 ml/L of HF (49%) solution for 5 min.
3) Ni deposition (100 nm) on the surface of the polymeric fibers:
Immersion in 7.5g/L of $NiSO_4.6H_2O$, 7.5 g/L $Na_2HPO_2.H_2O$, 30 g/L
$Na_3C_6H_5O_7.2H_2O$, NH_4OH (pH ≈ 8.0) at 80 °C solution for 10 min.
4) Surface deposition of Pd (100nm) by Ni displacement:
Immersion in 0.1 g/L of $PdCl_2$ and 50 ml/L of HF (49%) solution for 10 min.
5) Surface passivation with diamond like-carbon deposition (DLC: 5µm): The deposition was carried out in a HDPECVD reactor with a flow rate of 25 sccm methane. 440 W was applied to the coil and 150 W to the electrode with a 11 kV voltage. The deposition rate was 1.3 microns in 5 min and the process were carried out during 20 min.

The electroless process was performed in accordance with the following sequence: first, the fibers mat was immersed in a stannous activation solution in order to prepare the fiber surface to react with the palladium solution (steps 1 and 2).

Second, the structure was immersed in the nickel solution in order to have a continuous metallic layer over the fiber (step 3). Following, the sample was immersed in a palladium solution again in order to displace nickel and completely cover the fibers with a palladium film.

Finally, a DLC layer, 5 µm thick, was deposited in a homemade apparatus to passivate the surface of the Pd in order to avoid humidity adsorption and stabilize the background resistance of the fibers recovered with Pd.

The complete coating of the fibers was confirmed by RBS and SEM analysis.

III. Results of Fibers Characterization

Fig. 4 shows the SEM image obtained from the sample after palladium deposition and after the DLC deposition. The fibers are totally covered by Pd as shown in figure 4 a) and the typical fiber diameter was 484 nm. Figure 4 b) confirms that the DLC layer covers the fibers and the typical fiber diameter were 1500 nm.

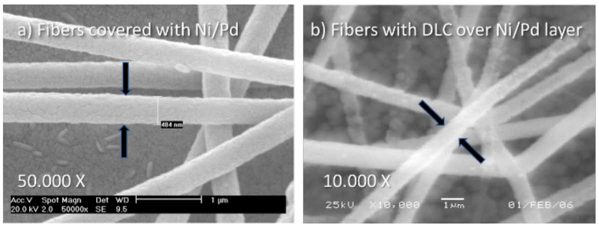

Fig. 4 - Fibers covered with Pd: (a) before passivation with DLC and (b) after passivation with DLC.

Fig. 5 shows the RBS spectra confirming the presence of Si, Ni and Pd on the sample. The Pd signal appears in the corresponding surface channel according to the energy used in the analysis. Also, the Ni appears dislocated from the corresponding surface channel suggesting that all the Ni atoms in the surface was replaced by the Pd. Thus, we can say that fiber is completely covered by a Pd layer.

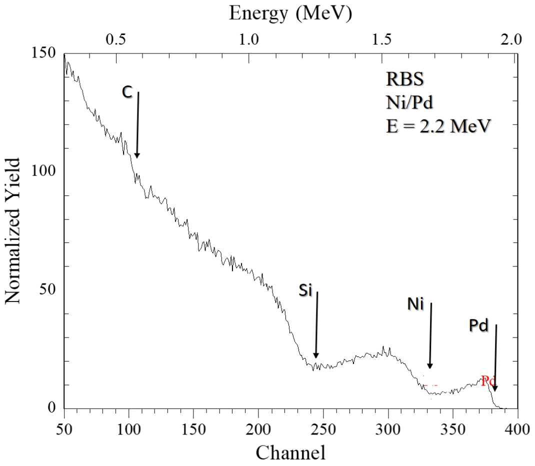

Fig. 5 - RBS spectra with the corresponding channels for Si, Ni and Pd in the sample.

IV. Results of Hydrogen Sensing

The response of the prototype to temperature variation and residual gas concentration in the environment was tested. The response tests were performed using an ultrapure gas mixture with different hydrogen concentrations in 1.5L/min argon (50, 100, 150 and 200ppm) having as starting point Ar+0.01%H_2 (100ppm of H_2). All the sensor response tests were done in an RTP furnace adapted to control the flow of H_2 as shown in Fig.6.

The sensor samples were placed in the RTP furnace onto a 4-inches wafer where the temperature was controlled in the range of 0 to 100^{o}C and the system was purged with argon flow until there is no variation in the resistance of the sensor under test.

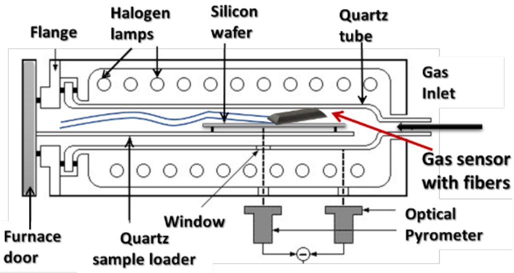

Fig. 6 - RTP furnace setup showing the input of the gas mixture and halogen lamps to control the sensor temperature.

At first, it was tested sensors without DLC passivation. The time to reach 100°C from room temperature was approximately 300 min. The sensor takes about 10 min to cool down to the room temperature (~20°C).

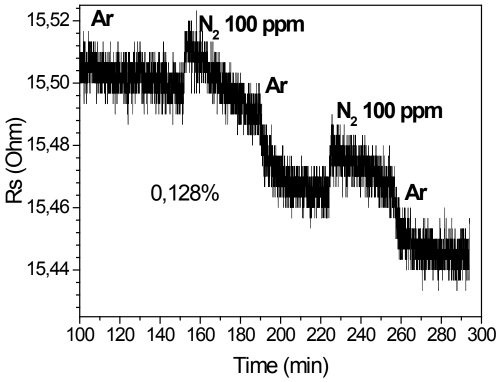

Fig. 7 - a) sensor response to the presence of H_2, b) extended region of figure 7a detailing the response to H_2.

Fig. 7 shows the results from tests performed at room temperature and with a concentration of 100 ppm of H_2. The measurement of the variation of the resistance of the sensor in presence of hydrogen in the environment was conducted as follows: After the first injection of hydrogen is observed a variation in the resistance of 0.128%, in this case, the sensor was not stabilized yet and takes about 300min for the absolute resistance to reach a constant value of 15.44 Ω. It was done two more injections of $H_{2,}$ and a good resistance variation was observed, indicating that the sensor responds to a small hydrogen concentration of 100ppm.

Since the stabilization of the absolute resistance takes about 300min in argon, it was deposited a passivation layer of DLC over the fiber mesh aiming at diminishing this time. As a result, it takes about 70min to stabilize meaning a substantial decreasing for a reference environment of argon (1.5 L/min.). This decrease was attributed to the lower content of adsorbed water of the DLC passivated samples.

To prove this hypothesis, the sensor sample was also submitted to nitrogen, argon and atmospheric air. It is noteworthy in Fig. 8 that the absolute resistance slightly increases when the environment is changed from argon to atmospheric air and slightly decreases when the environment is changed from N_2 (100ppm of H_2O and O_2) to dry Ar. In both cases, the Ar presents lower content of water vapor and oxygen and, as a result, there exist lower absorption of water which is associated with the lowest value of absolute resistance.

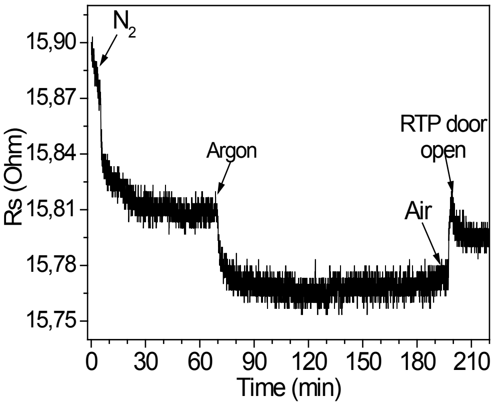

Fig. 8 - Influence of the environment on the sensor´s absolute resistance.

The DLC passivation layer adds a new interface to the system blocking the diffusion of water vapor and oxygen to the palladium film surface. The decreasing in the stabilization time suggests that this passivation layer acts as a filter and apparently allows only the diffusion of the hydrogen molecules favoring the mechanism of loss and gain of electrons by the hydrogen in the layer of palladium.

Fig. 9 illustrates the influence of the temperature on the absolute resistance in the range of 120 to 140ºC, for injections with a hydrogen concentration of 100ppm (Ar + 0,01%H_2) which is constant with the time. It is observed that the higher the temperature, the lower the absolute resistance. The experimental curve also shows that the time that the sensor takes to stabilize at each temperature is quite short, only a few seconds. Additionally, the sensor was kept at each temperature about 10 min. During each one of these time intervals, there was no significant variation of the resistance indicating that the sensor is very stable. Therefore, the temperature must be maintained fixed and controlled during the hydrogen detection.

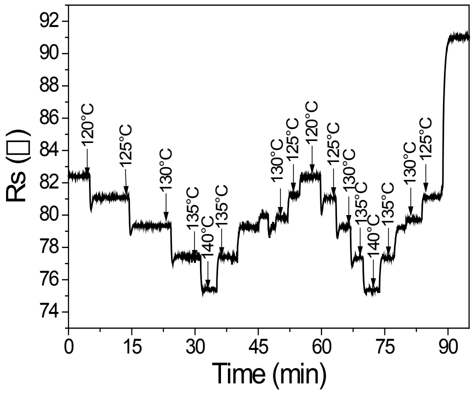

Fig. 9 - Temporal evolution of the absolute resistance for temperatures in the range of 120 and 140ºC.

In addition, Fig. 10 shows the same absolute resistance as a function of the temperature, revealing that it varies linearly with the temperature.

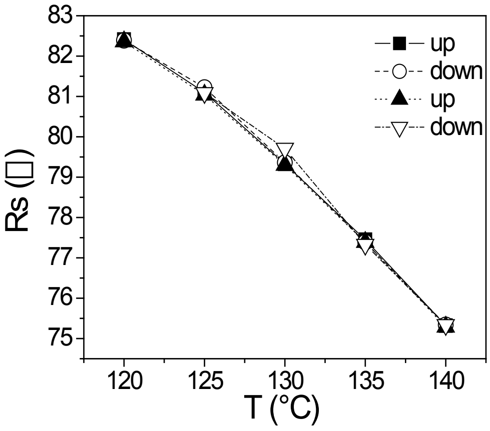

Fig. 10 - Absolute resistance as a function of the temperature in the range of 120 to 140ºC.

Fig. 11 shows the relative variation of the resistance at room temperature (25ºC) for a hydrogen concentration of 100ppm (Ar + 0.01%H_2). The sensor was subjected to multiple injections of Ar and H_2 (100ppm) at time intervals of 10 min in order to verify the reproducibility and response to rapid changes in concentration without any parasitic influence in the obtention of ΔR/R since a four point approach was employed for resistance measurement [2]. It was observed that the sensor response was reproducible. The value of ΔR/R was (0.19±0.05)%. The rise time after H_2 injection was 75s and the fall time after Ar injection was 71s.

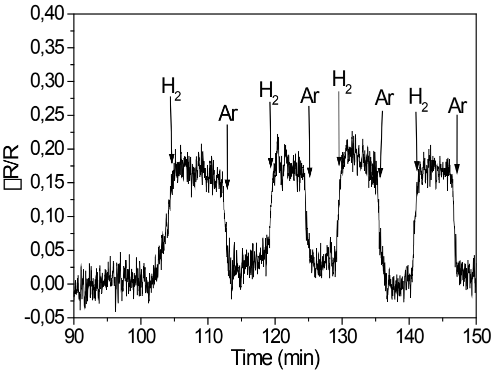

Fig. 11 - Multiple injections of Ar and H_2 (100ppm) at time intervals of 10 min.

Fig. 12 summarizes the relative resistance response (%) as a function of the temperature. It is noteworthy that the higher the temperature, the lower the response which is in agreement with the results described in the literature where the formation of palladium hidrides is possibly degrading the relative resistance response (ΔR/R) as the temperature is increased [2, 22].

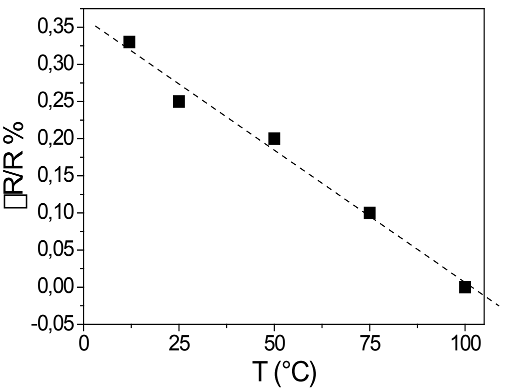

Fig. 12 - Relative resistance response (%) as a function of the temperature for 100 ppm of H_2.

Fig. 13 shows the relative resistance response (ΔR/R) for cycling times of 5 min for different partial pressures of hydrogen by diluting Ar+0.01%H_2 in pure argon as follows: 100ppm: 50sccm or 200sccm of Ar+0.01%H_2; 75ppm: 150sccm of Ar+0.01%H_2 and 50sccm of Ar; 50ppm: 100sccm of Ar+0.01%H_2 and 100sccm of Ar; 25ppm: 50sccm of Ar+0.01%H_2 and 150sccm of Ar. As a result, good reproducibility was obtained for each cycle during several weeks. In addition, Fig. 14 shows the relative resistance response (%) as a function of the hydrogen concentration at 75°C. The observed feature is consistent with the Lundstrom´s model represented by Eq 1 for $k(T)\sqrt{C_{H2}} < 1$.

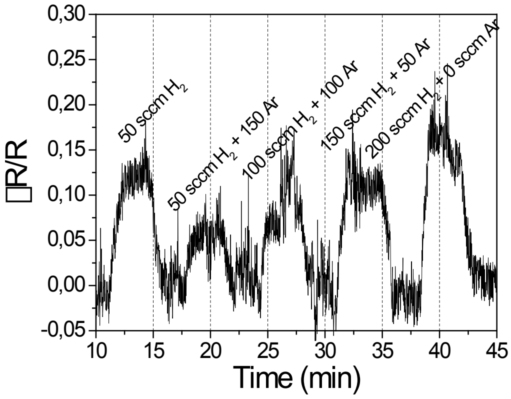

Figure 13 - Relative resistance response (%) at 75°C.

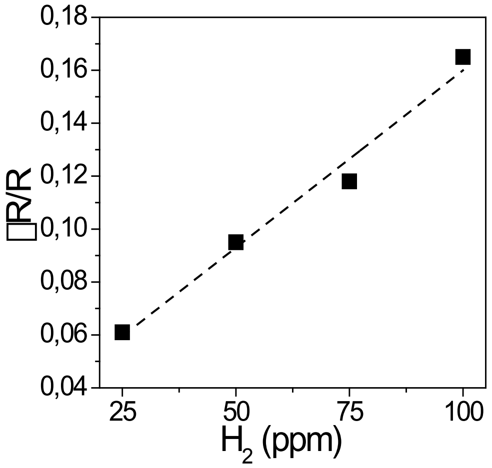

Figure 14 - Relative resistance response (%) as a function of the hydrogen concentration at 75°C.

The relative resistance increases linearly with the concentration and also the graph shows that the sensor was sensitive to concentrations of H_2 as small as 50 ppm indicating that the proposed sensor is sensitive to residual concentrations of H_2 compared to electrospun Pd-doped nanofibers encountered in the literature [2].

V. CONCLUSIONS

It was presented a gas sensor with a sensitive layer based on polymeric fibers covered with palladium deposited by electroless technique. The polymer fibers were electrospun over a gold comb structure with a distance between fingers of 50 µm. The results confirm that the hydrogen sensor was reproducible. The best relative resistance response was 0.35% for H_2 concentration of 100ppm under a controlled temperature of 25°C, which means that the large area offered by the mat of nanofibers combined with the properties of palladium resulted in a sensor capable of measuring residual concentrations of hydrogen.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Dr. Adir José Moreira for the SEM analysis and to Dr. Ronaldo Mansano for the DLC layer deposition.

REFERENCES

[1] C. Chen, Y. Tang, B. Vlahovic, F. Yan, "Electrospun polymer nanofibers decorated with noble metal nanoparticles for chemical sensing", Nanoscale Research Letters, 12, 2017, 451.

[2] A. Nikfarjam, S. Fardindoost, A. I. Zad, "Fabrication of Pd doped WO_3 nanofiber as hydrogen sensor," *Polymers*, 5, 2013, 45-55.

[3] M. F. Cabanas, "Insulation fault diagnosis in high voltage power transformers by means of leakage flux analysis," *Progress In Electromagnetics Research*,114, 2011, 211-234.

[4] G.-M. Ma, C.-R. Li, Y.-T. Luo, R.-D. Um, L. Wang, "High sensitive and reliable fiber Bragg grating hydrogen sensor for fault detection of power transformer*," Sensors and Actuators B: Chemical*, 169, 2012, 195-198.

[5] V. Polishchukab, E. Souteyranda, J.R. Martina, V.I. Strikhab, V.A. Skryshevskyab, "A study of hydrogen detection with palladium modified porous silicon," Analytica Chimica Acta, 375, 1998, 205-210.

[6] L. R. Jordan, P. C. Hauser, "Electrochemical Sensor for Acetylene," *Analitical Chemistry*, 69, 19, 1997, 2669-2672.

[7] S.I.A. Razak, I.F. Wahab, F. Fadil, F.N. Dahli, A.Z.M. Khudzari, H. Adeli, "A review of electrospun conductive polyaniline based nanofiber composites and blends: processing features, applications and future directions," Advances in Materials Science and Engineering, 2015, 2015, 356286, 1-19.

[8] Z.M. Huang, Y.-Z. Zhang, M. Kotari, S. Ramakrishna, "A review on polymer nanofibers by electrospinning and their applications in nanocomposites," *Composites Science and Technology*, 63, 2003, 2223-2253.

[9] A. Arinstein, Electrospun Polymer Nanofibers, Pan Stanford-CRC Press, New York: 2017, 208.

[10] W. E. Teo, S. Ramakrishna, "A review on electrospinning design and nanofiber assemblies," *Nanotechnology*, 17, R89 2006.

[11] A. Camposeo, D. Sapadaro, D. Magri, M. Moffa, P.G. Gucciardi, L. Persano, O.M. Maragò, D. Pisignano, "Surface-enhanced Raman spectroscopy in 3D electrospun nanofiber mats coated with gold nanorods," Analytical and Bianalytical Chemistry, 408, 2016, 1357-1364.

[12] B. Ding, M. Wang, J. Yu, G. Sun, "Gas sensors based on electrospun nanofibers," Sensors, 9, 2009, 1609-1624.

[13] X. Shi, W. Zhou, D. Ma, Q. Ma, D. Bridges, Y. Ma, A. Hu, "Electrospinning of nanofibers and their applications for energy devices," Journal of Nanomaterials, 2015, 2015, 140716, 1-20.

[14] D. Saraiva Gomes, A.N.R. da Silva, N.I. Morimoto, L. T.F. Mendes, R. Furlan, I. Ramos, "Characterization of an electrospinning process using different PAN/DMF concentrations," *Polímeros (São Carlos. Impresso)*, 17, 2007, 206-211.

[15] A. N. R. da Silva, M. L. P. da Silva and E. R. Fachini, "Nanofibers and thin films as a selective membrane for sensors and microTAS," *Journal of Physics: Conference Series*, 421, 2013, 012013.

[16] D. Saraiva Gomes, A. N. R. da Silva, "The incorporation of carbon black particle into electrospun nanofiber" in 29th Symposium on Microelectronics Technology and Devices (SBMicro).

[17] D. Aussawasathien, J.-H. Dong, L. Dai, "Electrospun polymer nanofiber sensors," Synthetic Metals, 154, 2005, 37-40.

[18] F. Wang, H. Gu, T.M. Swager, "Carbon nanotube/ polythiophene chemiresistive sensors for chemical warfare agents," Journal American Chemical Society,130, 16, 2008, 5392-5393.

[19] N.J.Pinto, "Electrospun conducting polymer nanofibers as the active material in sensors and diodes," Journal of Physics: Conference Series", 421, 2013, 012004.

[20] J. Huang, T. You (2013). Electrospun Nanofibers: From Rational Design, Fabrication to Electrochemical Sensing Applications, Advances in Nanofibers, Dr. Russel Maguire (Ed.), InTech, DOI: 10.5772/57099. Available from: https://www.intechopen.com/ books/advances-in-nanofibers/electrospun-nanofibers-from-rational-design-fabrication-to-electrochemical-sensing-applications

[21] L. Han, A. Andrady, K. Guzan, D. Ensor, "Electrospun Composite Nanofibers for Sensor Applications," in *MRS Proceedings*, 2009, doi:10.1557/PROC-1240-WW09-27, 1240.

[22] Christofides C., Mandelis, A. Solid-state sensors for trace hydrogen gas detection., *Journal of Applied Physics*, 68, 6, 1990, R1-R30.

[23] Lundström, K. I., *Sensors and Actuators*, 1, 403 (1981).