Effect of displacement on resistance and capacitance of polyaniline film

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This paper investigates the properties of displacement sensors based on polyaniline (PANI) films. About 1 wt% of PANI micropowder is mixed and stirred in a solution of 90 wt% water and 10 wt% alcohol at room temperature. The films of PANI are deposited from solution by drop-casting on Ag electrodes, which are preliminary deposited on glass substrates. The thicknesses of the PANI films are in the range of 20 μm–80 μm. A displacement sensor with polyaniline film as an active material is designed and fabricated. The investigations showed that, on average, the AC resistance of the sensor decreases by 2 times and the capacitance accordingly increases by 1.6 times as the displacement changes in the range of 0 mm–0.5 mm. The polyaniline is the only active material of the displacement sensor. The resistance and capacitance of the PANI changes under the pressure of spring and elastic rubber, and this pressure is created by the downward movement of the micrometer.

Keywords: polyaniline, displacement, sensor, resistance and capacitance

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1. Introduction

There are different types of displacement sensors that have commonly been used with the following sensing modes: capacitive, eddy-current, linear variable differential transformer (LVDT), multiple resistor, optical instruments, photoelectric sensor and resistance potentiometers.[1,2] These sensors usually cover a long range of displacement from microns up to centimeters as well. Some of the sensors are non-contacting types, such as capacitive, eddy-current and photoelectric, while others are contacting types, such as LVDT, multiple resistor and resistance potentiometers.[1]

Cantilever-type displacement sensors using diffused silicon strain gauges based on two kinds of alloys have been developed by Mitsuo *et al.*[3] A new device has been designed, and a prototype has been built and tested, that can simultaneously measure the displacements and/or the components of a force in three orthogonal directions. This three-dimensional (3D) sensor consists of four/eight strain gauges attached to the four arms of a single cross-shaped force-measuring cantilever spring.[4] The resistance–displacement characteristic of a magneto-resistor moving in a magnetic field was examined by Ferris *et al.*[5]

As is known, polyaniline (PANI) is one of the most interesting conducting polymers due to its good conductivity, stability, easy preparation and potential applications for the fabrication of different organic semiconductor devices.[6–8] The fabrication of the displacement sensor and investigations of the squeezing effect to the PANI would be useful from a practical point of view and for the deepening of knowledge about the physical properties of the polymer. It would be reasonable to investigate the resistance–displacement and capacitance–displacement relationships. In continuation of our efforts in fabrication and our investigation of the different kinds of sensors based on organic semiconductors,[9–11] we report here the design, fabrication and investigation of the sandwich-type resistance and capacitance–displacement sensors based on polyaniline films.

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2. Experimental

The emeraldine base PANI commercially available from Sigma Aldrich with formula ($C_{24}H_{20}N_4$) and a molecular weight ∼20000 was used. The molecular structures of the PANI are shown in Fig. 1, where $n = m = 0.5$. The 1 wt% of PANI powder was mixed in a solution of 90 wt% water and 10 wt% alcohol and stirred at room temperature. Glass substrates were cleaned for 10 minutes by using distilled water in an ultrasonic cleaner and then dried. Then the substrates were also plasma cleaned for 5 min. The Ag thin film electrodes were deposited by vacuum evapouration on cleaned substrates. The thickness and the size of the Ag electrodes was 100 nm, 10 mm×10 mm respectively. The PANI's films with thickness ranging from 20 μm–80 μm were deposited from solution by drop-casting on Ag electrodes at room temperature.

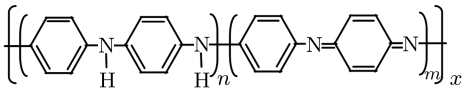


Fig. 1. Molecular structure of the PANI.

Figure 2 shows a scanning electron microscope (SEM) image of PANI film that was obtained by a Philips XL-30 SEM. It can be seen that the structure of the film is not uniform and contains clusters of the PANI particles. The sizes of the clusters are in the range of 5 μm–15 μm.

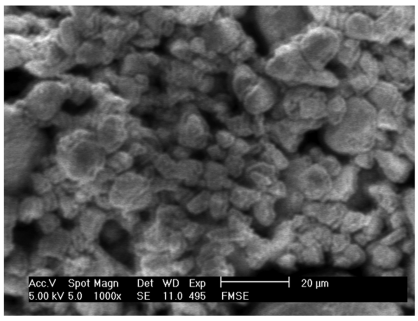


Fig. 2. SEM image of the PANI film.

The fabricated sensors were kept at room temperature for one night to evapourate the moisture from the films. To make a sandwich-type Ag/PANI/Al resistance and capacitance displacement sensor (Fig. 3), thin aluminum foil of thickness 40 μm and size 5 nm × 5 mm was used as a second electrode. The sensor consists of the following elements: glass substrate 1, silver film 2, PANI film 3, aluminum foil 4, terminals 5 and 6, elastic rubber 7 with 2-mm height and 6-mm diameter, spring 8 having 3-mm height and 5-mm diameter, and micrometer 9. The value of the displacement was measured by micrometer. As the micrometer moves down in the vertical direction, the value of the displacement increases. The range of the displacement depends upon the heights of the spring and elastic rubber (Fig. 3) and the elastic properties of their materials. The capacitance C and the resistance (or dissipation D) were measured at a frequency of 120 Hz by using an ESCORT ELC-132A handheld LCR meter. Depending on the value, the resistance R was measured directly or calculated by the measurement of dissipation by the following expression[12]

$$R = 1/2\pi fCD, \tag{1}$$

where f is frequency.

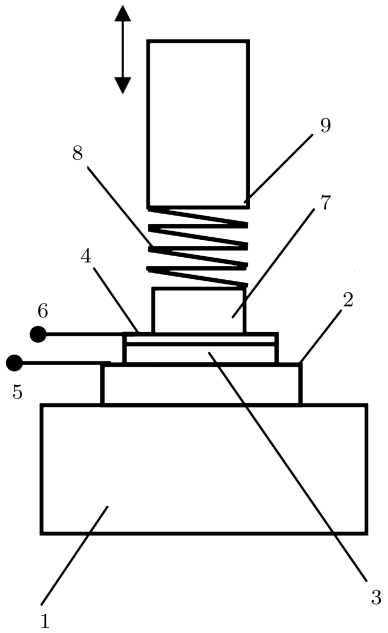


Fig. 3. Ag/PANI/Al resistance and capacitance displacement sensor: glass substrate 1, silver film 2, PANI film 3, aluminum foil 4, terminals 5 and 6, elastic rubber 7, spring 8, and micrometer 9.

3. Results and discussion

Figure 4 shows the relative resistance–displacement and capacitance–displacement relationships of the Ag/PANI/Al sensor. It can be seen that with an increase in the displacement from 0 to 0.5 mm, the sensor's resistance decreases by 2 times and its capacitance increases by 1.4 and 1.8 times for PANI films of 20 μm and 80 μm, respectively.

The sensor's resistance R can be represented by the following expression,[13]

$$R = d\rho/A = d/\sigma A, \tag{2}$$

where d is the length or inter-electrode distance and A is the cross section of the sample (in this case the area of the aluminum electrode), and ρ is resistivity ($\rho = 1/\sigma$, where σ is conductivity). The resistance–displacement relationship shown in Fig. 4 may be due to a decrease in the thickness d of the film under the effect of squeezing by the micrometer and/or an increase in the conductivity σ of the composite due to a decrease in the distances between the PANI molecules (Eq. (2)). It can be assumed that the last process dominates.

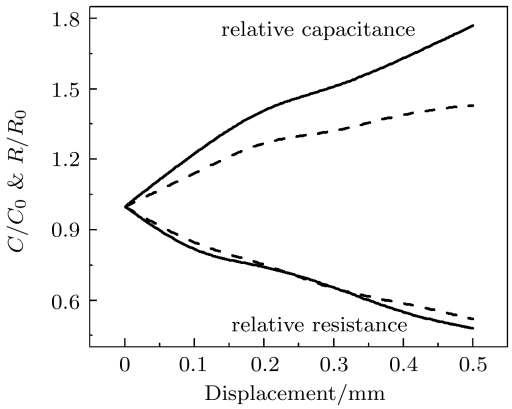


Fig. 4. Relative resistance–displacement and capacitance–displacement relationships for the Ag/PANI/Al sensor: PANI films thickness is 80 μm (solid line) and 20 μm (dashed line).

For the simulation of the experimental results (Fig. 4), the following exponential function[14] can be used,

$$f(x) = \mathrm{e}^{-x}. \tag{3}$$

For the present case, equation (2) can be represented in the following expression,

$$R/R_0 = \mathrm{e}^{-DK_1}, \tag{4}$$

where D is displacement, and K_1 is the resistance displacement factor. From the experimental data shown in Fig. 4, the displacement factor K_1 was determined ($K_1 = 1.386\ \mathrm{mm}^{-1}$) for a displacement of 0.5 mm.

Figure 5 shows experimental (from Fig. 4) and simulated (by Eq. (3)) graphs. It can be seen that the simulated curve is matched reasonably with the experimental data.

The decrease in the sensor's resistance with an increase in the displacement can be explained as follows. The mechanism of conductivity in PANI can be considered as thermally assisted hopping transitions between spatially separated sites, molecules that can be attributed to the percolation theory.[15,16] According to percolation theory, the average conductivity σ of the material can be found by the expression

$$\sigma = \frac{1}{LZ}, \tag{5}$$

where L is a characteristic length, depending on the concentration of the sites, and Z is the resistance of the path with the lowest average resistance. With an increase in the displacement, the PANI film will be squeezed between silver film and aluminum foil (Fig. 3). This squeezed film may cause, firstly, a decrease in L and, secondly, lowering of Z. As a result, the conductivity of the sample increases and the resistance decreases accordingly, as observed experimentally (Fig. 4).

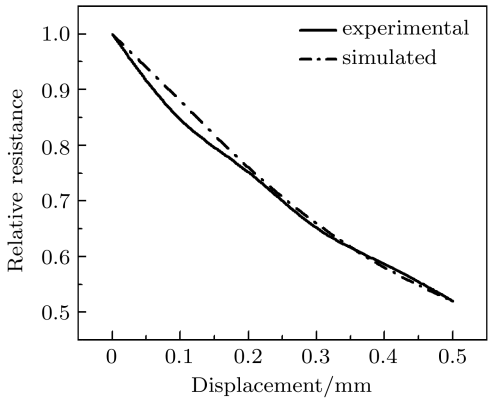


Fig. 5. Comparison of experimental and simulated relative resistance–displacement relationships for the Ag/PANI/Al displacement sensor.

The room temperature AC capacitance of the Ag/PANI/Al sensors was in the range of 0.02 nF–0.3 nF at zero displacement. The sensor's capacitance C can be represented by the following expression, [13]

$$C = \varepsilon\varepsilon_0 A/d, \tag{6}$$

where A is the area of the capacitor, ε is the relative permittivity, ε_0 is the permittivity of free space and d is the distance between plates of the capacitor. The capacitance–displacement relationship shown in Fig. 4 may be due to (i) a decrease in the thickness d of the PANI film under the pressure of the micrometer and/or (ii) an increase in the relative permittivity of the PANI film, which is due to (a) the decrease in distances between the molecules (Eq. (4)) and (b) a change in its polarizability. We consider that the contribution of the last process dominates in the change of capacitance of the sensor due to a change in displacement.

For the simulation of the experimental capacitance–displacement relationships for the

Ag/PANI/Al sensor (Fig. 4), the following phenomenological expression[17] can be used,

$$C/C_0 = (\varepsilon_s/\varepsilon)^n, \tag{7}$$

where ε and ε_s are the permittivity coefficients of the PANI film at normal and squeezed states, respectively, and C_0 and C are the corresponding capacitances. The factor n is related to the morphology of the material. Equation (7) can be represented as

$$C/C_0 = (\varepsilon_s/\varepsilon)^n = (1 + K_2 D)^n, \tag{8}$$

where

$$\varepsilon_s = \varepsilon(1 + K_2 D), \tag{9}$$

with K_2 being the capacitance displacement factor.

Figure 6 shows experimental (from Fig. 4) and simulated (by Eq. (8)) graphs in the case of $n = 0.5$ and $K_2 = 4.27$ mm^{-1}. It can be seen that the simulated curve is matched reasonably with the experimental data.

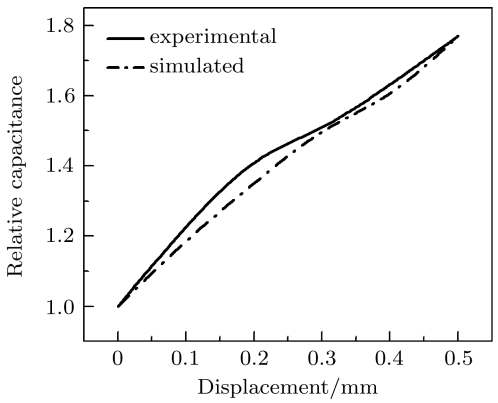


Fig. 6. Comparison of experimental and simulated relative capacitance–displacement relationships for the Ag/PANI/Al sensor.

In Figs. 5 and 6, deviation of the simulated graphs from the experimental graphs in the range of lower displacement may be firstly due to the complexity of the structure of the PANI films (Fig. 2). Secondly, equation (3), (4) and (7) can probably be used in the first approximation only and these equations can be replaced by series.[14]

Figures 4–6 show resistance and capacitance dependence on total displacement measured by the micrometer. The total displacement is the sum of the displacements of the spring (8 in Fig. 3), elastic rubber (7 in Fig. 3) and PANI film (3 in Fig. 3). The largest displacement values are concerned with the displacement of the spring (8 in Fig. 3) and elastic rubber (7 in Fig. 3). Displacement of the PANI film (3 in Fig. 3) can be considered lowest, as the modulus of elasticity of this material is definitely larger than that of the elastic rubber. The PANI is the only active material of the displacement sensor. The resistance and capacitance of the PANI change under the pressure of the spring and elastic rubber, and this pressure is created by the downward movement of the micrometer. Probably, the key factors for the performance of the sensor are the following: size of PANI clusters (Fig. 2), solution preparation technique (solvent composition, time of stirring, temperature, etc.), film thickness, and size and properties of the spring and elastic rubber. We can assume that the decrease in the height of the spring or elastic rubber will make the graphs shown in Figs. 4–6 steeper and *vice versa*. The detailed investigation of these parameters will be a matter for future work.

The large-area flexible pressure sensor matrix with organic field-effect transistors based on pentacene were fabricated by Someya *et al.*[18,19] and it was found that the matrix shows high pressure sensitivity and mechanical flexibility. The fabricated displacement sensor, with PANI based resistance/capacitance sensing film, can be used as a pressure sensor as well if the pressure is applied to the spring (8 in Fig. 3) downward in a vertical direction. As experimental curves of relative resistance–displacement (Fig. 4) and relative capacitance–displacement relationships for the Ag/PANI/Al sensor are non-linear, these graphs can be linearized by nonlinear op-amps.[20]

4. Conclusion

The sandwich-type resistance and capacitance Ag/PANI/Al displacement sensor was designed, fabricated and investigated. It was found that with an increase in displacement, resistance of the sensor decreases and capacitance increases. The resistance–displacement and capacitance–displacement relationships were simulated. To explain the conduction mechanism, the percolation theory is used. The PANI system is assumed to be a polymer system that shows high sensitivity towards the effect of squeeze.

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References

[1] Dally J W, Riley W F and McConnell K G 1993 *Instrumentation for Engineering Measurements*, 2nd edn. (New York: John Willey & Sons Inc.)

[2] Simpson C D 1996 *Industrial Electronics* (New Jersey: Prentice Hall Inc.)

[3] Ai M, Shimazoe M, Soeno K, Nishihara M, Yasukawa A and Kanda Y 1981–1982 *Sens. Actuators* **2** 297

[4] Kristiansen K, McGuiggan P, Carver G, Meinhart C and Israelachvili J 2008 *Langmuir* **24(4)** 1541

[5] Ferris S A, Ivison J M and Walker D 1970 *J. Phys.* E: *Sci. Instrum.* **3** 639

[6] Bhadra S, Khastgir D, Singha N K and Lee J H 2009 *Prog. Polymer Sci.* **34** 783

[7] Bejbouji H, Vignau L, Miane J L, Dang M T, Oualim El M, Harmouchi M and Mouhsen A 2010 *Solar Energy Materials and Solar Cells* **94** 176

[8] Mallick K, Witcomb M, Erasmus R and Strydom A 2010 *J. Appl. Polymer Sci.* **116** 1587

[9] Moiz S A, Ahmed M M and Karimov Kh S 2005 *ETRI J.* **27(3)** 319

[10] Moiz S A, Karimov Kh S, Gohar N D 2004 *Eurasian Chem. Technol. J.* **6** 201

[11] Moiz S A, Ahmed M M and Karimov Kh S 2005 *Jpn. J. Appl. Phys.* **44(3)** 1199

[12] Irwin J D 1999 *Basic Engineering Circuit Analysis,* 6th edn. (New York: John Wiley & Sons)

[13] Epifanov GI and Moma Y A 1986 *Solid State Electronics* (Moscow: V Shkola)

[14] Croft A, Davison R and Hargreaves M 1993 *Engineering Mathematics, a Modern Foundation for Electronic, Electrical and Control Engineers* (Great Britain: Addison-Wesley Publishing Company)

[15] Brabec C J, Dyakonov V, Parisi J and Sariciftci N S 2003 *Organic Photovoltaics, Concepts and Realization* (Berlin, Heidelberg: Springer-Verlag)

[16] Bottger H and Bryksin V V 1985 *Hopping Conductions in Solids* (Berlin: Akademie Verlag)

[17] Rittersma Z M 2002 *Sens. Actuators* A **96** 196

[18] Someya T, Sekitani T, Iba S, Kato Y, Kawaguchi H and Sakurai T 2004 *Proc. Natl. Acad. Sci.* (PNAS) *USA* **101** 9966

[19] Someya T, Kato Y, Sekitani T, Iba S, Noguchi Y, Murase Y, Kawaguchi H and Sakurai T 2005 *Proc. Natl. Acad. Sci.* (PNAS) *USA* **102** 12321

[20] Irvine R G 1994 *Operational Amplifiers Characteristics and Applications*, 3rd edn. (Englewood Cliffs, New Jersey: Prentice Hall)