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Short Communication

Deformable organic semiconductor sensors based on metal free phthalocyanine for pressure and compressive displacement monitoring

Muhammad Tariq Saeed Chani[1*], *Abdullah M Asiri*[1,2]

[1] Center of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia
[2] Department of Chemistry, King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia
[*]E-mail: mtmohamad@kau.edu.sa, tariqchani1@gmail.com

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Deformable differential semiconductor sensors of pressure and compressive displacement having two inputs and one output were fabricated. For the fabrication of the sensors the rubbing in technology was used to form conductive-semiconductive-conductive layered structure on a rubber substrate. The rubber substrate was doped with carbon nanotubes (CNTs) and mixture of CNTs-H2Pc (50:50 wt.% CNTs-metal free phthalocyanine) to form conductive and semiconductive layers, respectively. The dimensions of the rubber substrates were 2.5 x 1.5 x 0.5 cm^3. Thickness of the CNT and CNT- H_2Pc composites layers were in the range of 29-33µm, while their length and the width were 5-6 mm and 2-3 mm, respectively. It was found that the output resistance and the impedance of the sensor either decreased or increased depending on the input. The sensor showed high sensitivity of resistance and impedance under the effects of pressure (up to 240 gf/cm^2) and displacement (up to 500 µm). For practical applications the fabricated sensors may be used for determining pressure and compressive displacement.

Keywords: Organic semiconductors; Rubbing-in technique; Two points sensitivity; Impedance; Current-Voltage behavior, Resistance.

1. INTRODUCTION

Semiconductor sensors based on differential pressure-transmitters (DPT) were investigated by Matsuoka et.al [1]. Using diaphragm-type silicon sensors he devised a method for the sensing of DPT's body [2]. The semiconductor differential pressure measuring device was presented in ref. [3], and capacitive differential pressure sensor was investigated in ref. [4]. In ref. [5] the independent-excitation cross-coupled differential-pressure transducer was presented as well. The method for the measurement of differential pressure using removable pressure (differential) sensor was described in ref. [6]. A solid state sensor containing differential pressure-indicator (electrical visual) was presented by Monebaty [7]. Optical differential pressure transducer utilizing a bellows and flexure systems was presented in ref. [8]. Differential pressure measurement using backside sensing in a single ASIC was described in ref. [9]. In ref. [10] the reliable piezo-resistive pressure sensor's properties were discussed. Differential pressure sensor was presented in ref. [11]. Sarkar et.al [12] designed and developed a differential optical sensor (linear variable) for the measurement of linear displacement (small range). For displacement sensing a differential transformer (planar linear variable) was design and developed by Anandan et.al [13]. In ref. [14] a laser sensor for the displacement, distance and position measurements was described. In ref. [15] inductive displacement sensors were described.

For sensor applications the development of deformable structures that can retain their conducting properties are gaining much interest. The flexible and stretchable sensors based on carbon nanotubes (CNTs) film on natural rubber were fabricated by Takakaluru et.al [16]. The use of rubbing-in technique to embed the conducting and semiconducting powder in to rubber substrates in a specific pattern to make various devices has been described [17]. The rubbing-in technique has substantial advantages over other methods such as, stamping of CNTs as a pattern conductive electrode onto pre-stretched silicone layer [18] and the deposition of CNTs mixture on a substrate [19]. Such prior fabrication techniques weakness the surface coating rather than having an embedded composite structure within substrate's surface.

There is a growing need to provide different and more complex elastic and deformable devices. Deformable differential semiconductor sensors of pressure and compressive displacement having two inputs and one output were fabricated on the base of rubber-CNTs-H_2Pc composite using rubbing-in technology. The effect of displacement up to 500 μm and pressure up to 240 gf/cm^2 on the resistance and the impedance of the sensors were investigated.

2. EXPERIMENTAL

The powders of metal free phthalocyanine (H2Pc) and CNTs (carbon nanotubes) were purchased from Merck (https://www.sigmaaldrich.com/catalog/product/aldrich/253103) and Sun Nanotek Co. LTD (http://www.sunnano.com), respectively. The diameter of the multiwalled carbon nanotubes was 10 to 30 nm, while their length was in the range of 100 to 200 nm. The molecular weight of organic semiconductor metal free phthalocyanine ($C_{32}H_{18}N_8$) is 514.54 and its chemical structure is shown in Fig. 1.

The rubbing-in technique was used to fabricate the rubber based CNTs-H_2Pc composite sensor, which is illustrated in Fig.2. To form the composite the conducting/semiconducting layers, the powder is poured on to the stretched rubber substrate. A round shaped polished metallic block is used to rub the powder on the rubber surface using a special mechanism which controls the frequency and the direction of the block.

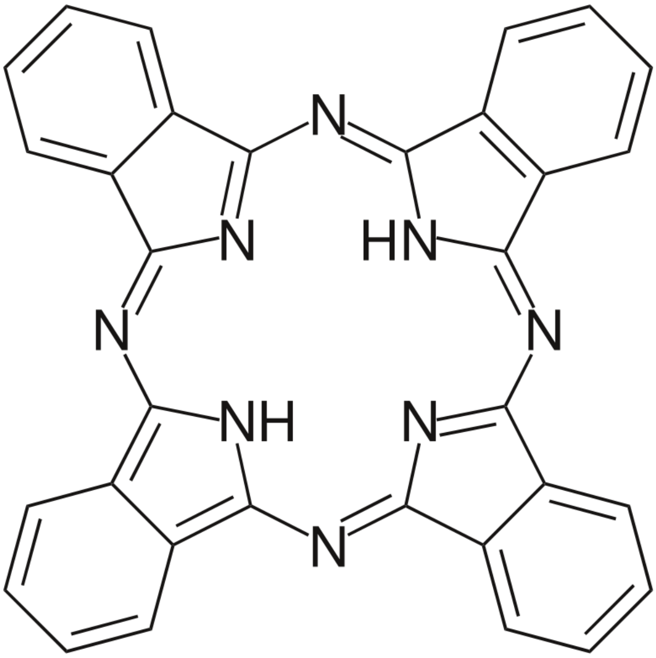

Figure 1. Molecular structure of organic semiconductor H_2Pc (metal free phthalocyanine)

In present case, by the selection of proper material, organic semiconductor metal free phthalocyanine, H_2Pc, where weak Van-der-Waals forces are available between molecules the pre-stretching of the rubber substrate was avoided, that is one of the technological advantages realized in this work. During this procedure the properly selected pressure is very important; this was kept 10gf/cm^2 to 20gf/cm^2. The frequency of the rubbing blocks varies from 10 to 20 Hz. The duration of the sample preparation was 15-20 s on average.

The CNT and CNT- H_2Pc composites films on rubber substrates were fabricated by rubbing-in technology (shown in Fig.2). The dimensions of the rubber substrates were 2.5 x 1.5 x 0.5 cm^3. In this process the rubber substrates were covered in the center uniformly by the mixture of CNT and H_2Pc powders (50:50 wt.%). On the edges the substrates were covered by the CNTs powder which played the role of electrodes. Thickness of the CNT and CNT- H_2Pc composites layers were in the range of 29-33µm, while their length and the width were 5-6 mm and 2-3 mm, respectively.

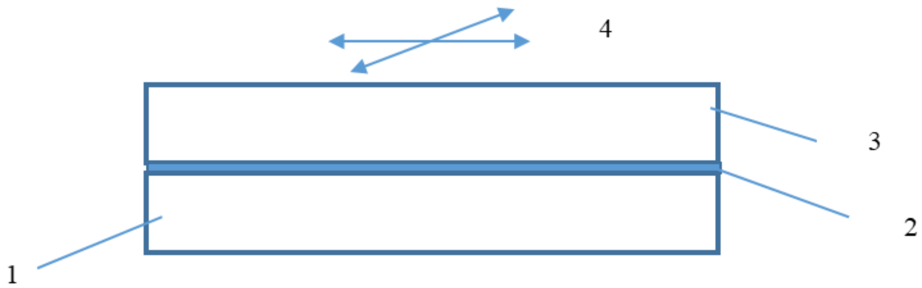

Figure 2. Schematic diagram of the sample fabrication by rubbing-in technology which can be used within the practice of the fabrication of organic semiconductor metal free phthalocyanine (H_2Pc) based sensor: rubber substrate (1), CNT and H_2Pc films (2), polishing rubber unit (3) and directions of the motion of the unit (4) in horizontal plane.

Figure 3 shows a schematic drawing of the sensor fabricated by rubbing-in technology. Total sizes of the deformable semiconductive sensor of pressure and compressive displacement were the following: 2.5x1.5x1 cm^3.

A digital multi-meter MT 4090 LCR was used for the measurement of resistance and impedance at 200 kHz. All the testing was done at room temperature and ambient environment. The samples were placed in special chamber when it was required. The compressive displacements (uniaxial) or pressure were applied on the rectangular prism sample along the length using the weights or micrometer mechanism in special experimental-arrangement. The processes of application of compressive forces or pressure on the rubber sample are shown in Fig. 3.

The fabricated sensors were tested by applying pressure or displacement on two points of the sensors (point 6 and point 7 as indicated in Fig.3).

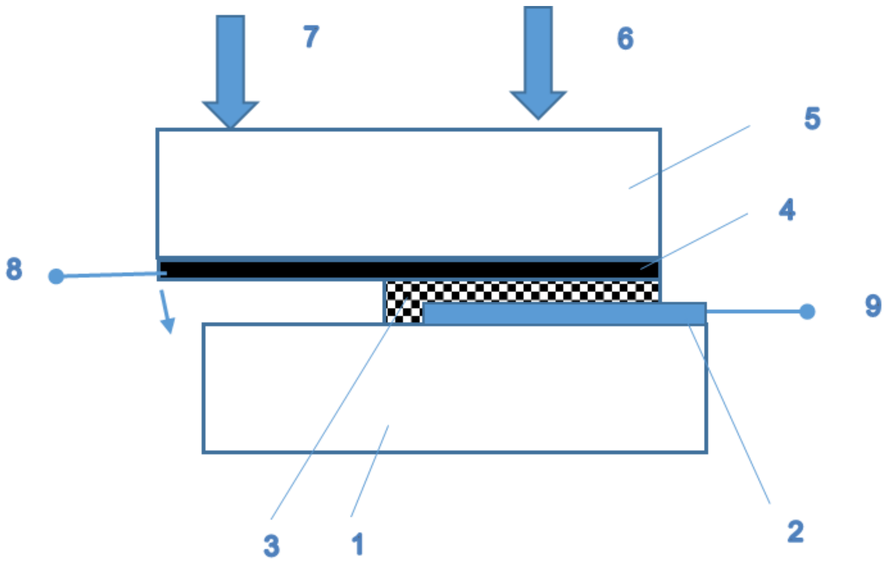

Figure 3. Schematic drawing of the fabricated deformable semiconductive sensor of pressure and compressive displacement by rubbing-in technology which can be used in practice: rubber substrate (1), CNT layer (2), CNT and H_2Pc composite layer (3), CNT layer (4), rubber cover (5), direct input for pressure or compressive displacement (6), side input for pressure or compressive displacement (7) and terminals (8 and 9) for the measurement of resistance and impedance.

3. RESULTS AND DISCUSSIONS

For the tranquil realization of the rubbing-in technology the proper selection of two materials on the base of their work functions plays an important role. Similarly, in electrochemistry the work function (or electrochemical potential) plays a crucial role in the selection of materials. Thus, from this point of view there are some similarities in the process which involve in electrochemistry and rubbing-in technology. Detailed information regarding this point of view may be found in the following articles [17, 20, 21].

Figure 4 shows the effect of pressure on the resistance and impedance (at 200 kHz) of the sensor when pressure is applied to input 6 (Fig.3). Both the impedance and resistance decrease with increasing pressure. The resistance/impedance-pressure relationship shows a near linear behavior. The increase in pressure up to 240 gf/cm^2 causes to decrease the resistance and impedance as well up to 1.56 and 1.57 times, accordingly. The rates of decrease in the resistance and impedance can be characterized by the following ratios [22]:

$$\Delta R/\Delta p = -11.6\ \Omega/(\mathrm{gf/cm^2}) \quad (1)$$

and

$$\Delta Z/\Delta p = -10.6\ \Omega/(\mathrm{gf/cm^2}) \quad (2)$$

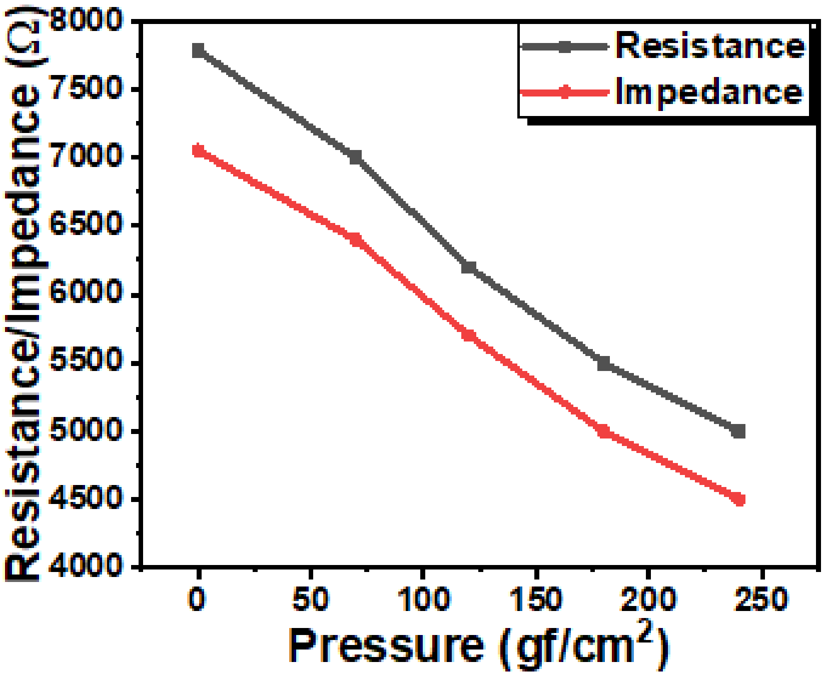

Figure 4. The dependences of the resistance and impedance (at 200 kHz) of the rubber, CNT and H_2Pc sensor on pressure applied to input 6.

Figure 5 shows the resistance/impedance-displacement relation of the sensor when the displacement is applied to input 6 (Fig.3). It can be observed that on increasing displacement the both impedance and resistance decrease in a quasi linear fashion. The increase in displacement up to 500 µm brings to decrease in the resistance and impedance as well up to 2.36 and 2.43 times, respectively. The rates of the decrease in resistance and impedance can be characterized by the following ratios:

$$\Delta R/\Delta d = -9.0\ \Omega/\mu m \quad (3)$$

and

$$\Delta Z/\Delta d = -8.3\ \Omega/\mu m \quad (4)$$

Figure 6 illustrates the dependences of the resistance and impedance (at 200 kHz) of the rubber, CNT and H_2Pc sensor on pressure when the pressure was applied to input 7. The application of pressure at input 7 causes to increase the resistance and impedance of the sensor. On increasing pressure up-to 240 gf/cm^2, the resistance and impedance increase up to 1.32 and 1.36 times, correspondingly. The rates of the increase of the resistance and impedance can be characterized by the following ratios:

$$\Delta R/\Delta p = 10.1\ \Omega/(gf/cm^2) \quad (5)$$

and

$$\Delta Z/\Delta p = 10.3\ \Omega/(gf/cm^2) \quad (6)$$

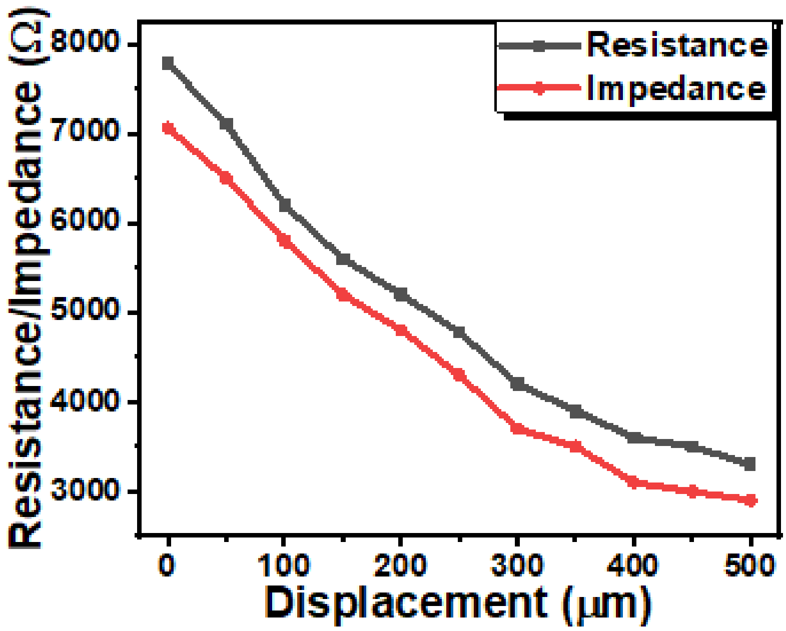

Figure 5. The dependences of the resistance and impedance (at 200 kHz) of the rubber, CNT and H_2Pc sample on compressive displacement (d) applied to input 6.

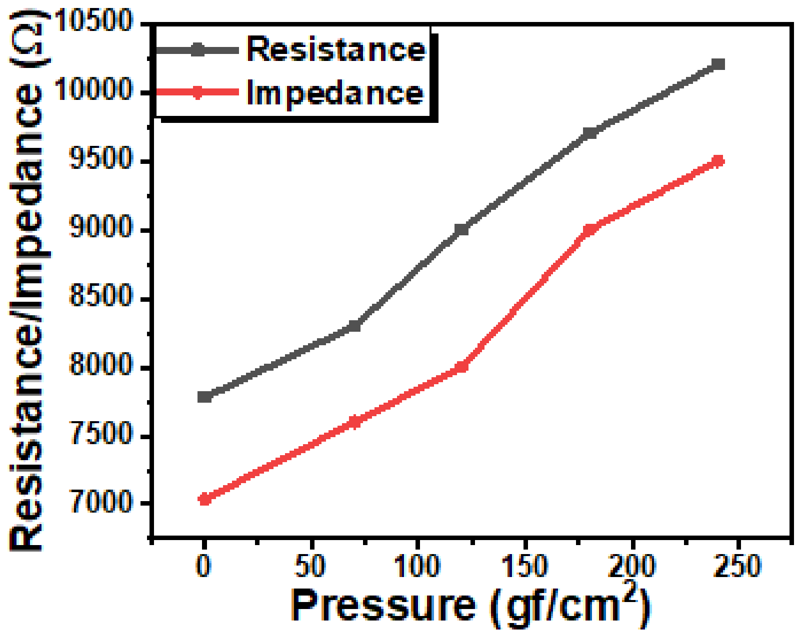

Figure6. The dependences of the resistance and impedance (at 200 kHz) of the rubber, CNT and H_2Pc sensor on pressure applied to input 7.

Figure 7 illustrates the dependences of the resistance and impedance (at 200 kHz) of the rubber, CNT and H_2Pc composite sensor on compressive displacement when the input is applied at input 7. The compressive displacement at point 7 causes to increase the impedance and resistance as well. As the displacement increases up to 500 μm impedance and the resistance increase by 2.27 and 2.15 times, respectively. The rates of the increase of the resistance and impedance can also be characterized by the following ratios:

$$\Delta R/\Delta d = 17.8\ \Omega/\mu m \quad (7)$$

and

$$\Delta Z/\Delta d = 17.9\ \Omega/\mu m \quad (8)$$

Physically the obtained results can be explained by the following way [23, 24]. Under the effect of pressure or compressive displacement at the input 6, the distances between the particles in rubber-CNT-H_2Pc composite decreased, the cross-section of the composite layer (Fig.3) increased. Moreover, the intermolecular and interatomic distances decreased that bring to decrease in the resistances and impedances that are seen in Fig.4 and Fig.5. The opposite phenomenon may take place when pressure or displacement is applied at input 7 that is seen in Fig.6 and Fig.7. The sensor is shockproof and can be used for the measurement of the pressure and compressive displacement.

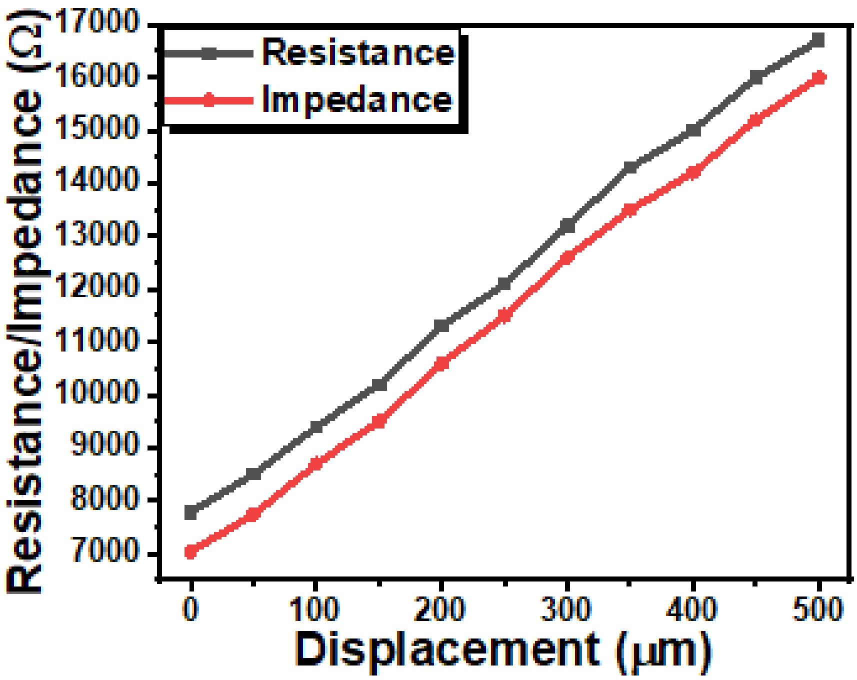

Figure 7. The dependences of the resistance and impedance (at 200 kHz) of the rubber, CNT and H_2Pc sensor on compressive displacement applied to input 7.

Figure 8 shows the current-voltage (I-V) characteristics of the deformable differential semiconductor sensor at different values of displacement: zero displacement d(0), forward displacement (+500 μm) and the reverse displacement (-500 μm). At zero displacement on applying 8.6 V input to the rubber-CNTs- H_2Pc composite based sensor the output current was 2 mA. The forward displacement of 500 μm on the same input voltage (8.6 V) causes to increase the output current up to 4.6 mA, while the reverse displacement of 500 µm cause to decrease output current up to 1.0 mA. The I-V characteristics of the fabricated sensors showed a quasi-linear behavior (Fig.8). The comparison of the properties of fabricated sensors with already reported pressure or displacement sensors is given in Table-1. It can be seen in Table-1 that the fabricated sensors give two outputs in response to single input.

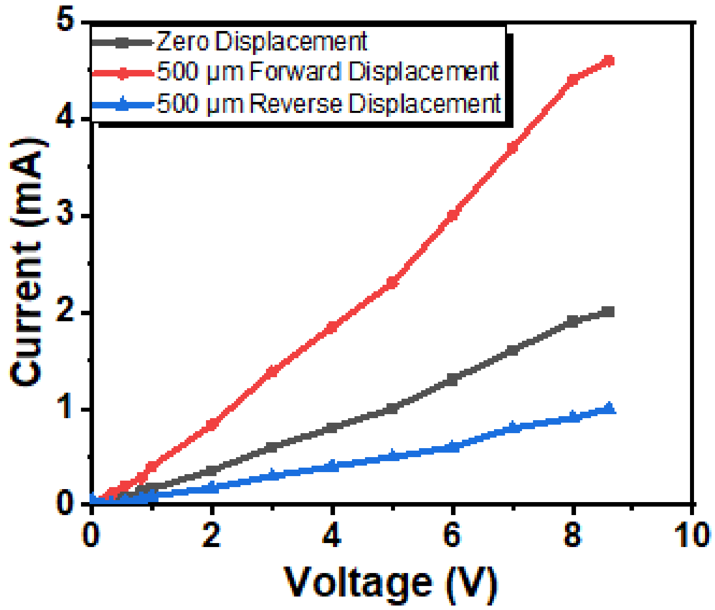

Figure 8. The I-V characteristics of the deformable differential semiconductor sensor at different values of displacement.

Table 1. Comparison of pressure and compressive displacement sensing properties of the fabricated sensors with recently reported sensors.

Sr. No	Fabrication Technology	Sensing Materials	Pressure Sensing		Displacement Sensing		Ref.
			Sensitivity (Ω cm^2/gf)	Sensing Range (gf/cm^2)	Sensitivity (Ω/µm)	Sensing Range (µm)	
1	Movable-electrode Sensor	CNT-Graphene			-0.17	0-100	[25]
2	Pressing	Paper-CNT			0.97x10^{-3} pF/µm	0-1000	[26]
3	Movable-electrode Sensor	CNT	645.2	0-1.86			[27]
4	Rubbing-in technique	Rubber-CNT-CNT+OD-Al	-424.2	0-33	-40.0	0-250	[28]
5	Movable-electrode Sensor	CNT-OD-Graphene	-30.0	0-100	-14.0	0-110	[29]
6	Pressing	CNT-Cu_2O	0.006	0-378			[24]
7	Rubbing-in technique	CNTs-H_2Pc	-11.6 +14.58	0-240	-8.8 +18.0	0-500	Current Study

In the fabricated sensors the rubber-CNTs- H_2Pc composite played the role of, firstly as a sensitive material and secondly, as a resistive material. This behavior is regarded to the much lower conductivity of H_2Pc as compared to the conductivity of the CNT. Due to its higher conductivity, the CNT played the role of contact materials as well. Overall, the resistances of fabricated CNT-(CNT+H_2Pc)- CNT sensors were sufficiently high in order to avoid or minimize the experimental errors related to connecting with sensor wires and resistances of CNT layers.

4. CONCLUSION

Deformable differential organic semiconductor sensor of pressure and compressive displacement with two inputs and one output was designed, fabricated and investigated using environmentally friendly organic material, semiconductor, metal free phthalocyanine (H_2Pc) and carbon nanotubes (CNT) by rubbing-in technology. For the fabrication of the devices by rubbing-in technology it was used low pressures because between the molecules of H_2Pc there are week Van der Waals forces only, that allows to use the technology at low pressures: 5-10 g/cm^2. Due to using organic semiconductor H_2Pc the film fabrication process was realized at low velocity (0.3-0.5) cm/sec that is economical and reliable. Changing ratio of the CNT and H_2Pc in the composite allowed to change initial resistance and impedances of the samples. Changing thickness of the CNT and H_2Pc in the composite allowed to change initial resistance and impedances of the samples as well. It was found that the output resistance and impedance of the sensor either decrease or increase depending on the influence of inputs. Deformable semiconductive devices fabricated by the use of environmentally friendly organic materials metal free phthalocyanine (H_2Pc) and carbon nanotubes (CNT) showed high sensitivity of the resistance and impedance at 200 kHz to uniaxial pressure and compressive displacement.

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