

# Flexible Pressure Sensors based on Screen-Printed P(VDF-TrFE) and P(VDF-TrFE)/MWCNTs

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**Abstract**—This paper presents large-area-printed flexible pressure sensors developed with an all screen-printing technique. The 4×4 sensing arrays are obtained by printing Polyvinylidene Fluoride-Trifluoroethylene P(VDF-TrFE) and their nanocomposite with multi-walled carbon nanotubes (MWCNTs) and are sandwiched between printed metal electrodes in a parallel plate structure. The bottom electrodes and sensing materials are printed sequentially on polyimide (PI) and polyethylene terephthalate (PET) substrates. The top electrodes with force concentrator posts on backside are printed on a separate PET substrate and adhered with good alignment to the bottom electrodes. The interconnects, linking the sensors in series, are printed together with metal electrodes and they provide the expandability of the cells. Different weight ratios of MWCNTs are mixed in P(VDF-TrFE) to optimize the percolation threshold for a better sensitivity. The nanocomposite of MWCNTs in piezoelectric P(VDF-TrFE) is also explored for application in stretchable interconnects, where the higher conductivity at lower percolation ratios are of significant importance compared to the nanocomposite of MWCNTs in an insulator material. To examine the functionality and sensitivity of sensor module, the capacitance-voltage analysis at different frequencies, and the piezoelectric and piezoresistive response of the sensor are presented. The whole package of foldable pressure sensor is completely developed by screen-printing and is targeted towards realization of low-cost electronic skin.

**Index Terms**— Screen Printing, Spin Coating, Polyvinylidene Fluoride Trifluoroethylene (PVDF-TrFE), Piezoelectric, Flexible Sensors

## I. INTRODUCTION

LARGE-area-printed electronics has gained interest recently and is emerging as an alternative to the conventional wafer based micro/nanofabrication technology, especially for applications requiring active/passive components on areas larger than the standard wafer size. Some of the attractive features of printed electronics are: large area coverage of sensors and electronics, simple processing of diverse materials, reduced material wastage, low fabrication cost and single patterned deposition techniques. As a result of commercial push, thus far the major research focus in the field of printed electronics has been on applications such as photovoltaics and displays. However, this is changing as active/passive

electronics is also needed in applications such as robotics skin. Various active/passive electronic components and devices are needed on flexible and large area substrates to develop electronic or tactile skin, which are of significant interest in robotics for safe human-robot interaction and other manipulation and exploration task [1-5]. The research in this paper describes one such work where printed electronics tools have been used to develop pressure sensor arrays.

The flexible pressure sensors arrays reported here are made from P(VDF-TrFE) and P(VDF-TrFE)-MWCNTs. The choice of these two materials is governed by that fact that common tasks by robots such as grasping, picking and placing an object from one place to another require capability to measure both static and dynamic contacts [2]. This is similar to human skin, which has specific mechanoreceptors to detect static and dynamic contact events. The piezoelectric materials such as P(VDF-TrFE) are known to detect dynamic contacts events such as pressure and contact force while picking an object. Similarly, the piezoresistive property of MWCNTs matrix in PDMS has been exploited to detect static events such as the contact force while holding an object [6]. Our work on pressure sensors based in these materials was presented in ASMC 2014 conference [7]. Extending the research further, we present in this paper the touch or pressure sensors made of P(VDF-TrFE)-MWCNTs composites. The combination of P(VDF-TrFE) and MWCNTs is explored with an intention to develop a pressure sensors which is capable of detecting both the static and dynamic contact forces, as the P(VDF-TrFE)-MWCNT nanocomposite is both piezoresistive (due to semi conductive network of MWCNTs) and piezoelectric (due to P(VDF-TrFE)) [8-10]. This property makes our sensors different from the PDMS-MWCNTs nanocomposite based sensors, which are primarily piezoresistive [11]. As shown in later sections, the new combination of P(VDF-TrFE) and MWCNT allows us to increase the bandwidth of sensors operation.

The solution based piezoelectric and piezoresistive tactile sensors are preferred as they can be printed on large areas and bendable substrates, which is needed for conformal covering of 3D surfaces such as a robot's body [12-15]. Further, printing of sensors is a low-cost approach. In this regard printed electronics route is appealing and the screen-printing is most attractive alternatives as it is closer to the manufacturing [7, 16, 17]. The

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simple processing steps, fast production of sensors, and uniform deposition of materials over large areas make screen-printing an attractive additive manufacturing method [18, 19]. Screen-printing has been used in this work to print piezoelectric and piezoresistive tactile sensors on flexible polymeric substrates. The focus of this paper lies in the manufacturing processes, ease of handling materials, compatibility of dissimilar materials in multilayer structures, overall assembly of the sensor modules and finally the type of sensors responding to normal compressive forces.

This paper is organized as follows: Section II briefly presents the state of the art relevant to the research presented in this paper. Section III describes synthesis of various solutions and the experiments performed. This is followed by presentation of results and discussions in sections IV. Finally, conclusions and future scope are given in section V.

## I. MATERIALS AND PROCESSES

### A. *P(VDF-TrFE)* for Pressure/Touch Sensors

The contact parameters such as temperature, proximity and pressure have been measured using sensors based on diverse transduction methods, including capacitive, piezoresistive and piezoelectric etc. [2, 20, 21]. The piezoelectric materials are unique as they allow us to measure dynamic touch or contact events and also enable multiple uses as sensors, actuators and energy harvesters [13, 22-24]. The piezoelectric materials used in these applications range from ceramics such as PZT and polymers such as Polyvinylidene fluoride (PVDF) and its copolymers. Generally, the ceramics such as PZT have higher piezo/pyroelectric constants and higher sensitivity than polymers, but the latter enjoy the advantage of mechanical flexibility and easy processing through solution deposition. For this reason PVDF and its copolymer such as *P(VDF-TrFE)* have been widely investigated for large area sensing. They also exhibit stable piezo, pyro and ferroelectric properties. Other attractive features of *P(VDF-TrFE)* are good pressure sensitivity, wide frequency response, cost effectiveness, ease of fabrication and light weight [25-28]. Fig. 1(a) shows a schematic of the piezoelectric based sensors in which the dipoles are aligned in parallel initially by poling and generate charges upon subjecting to a normal compressive force.

### B. *P(VDF-TrFE)-MWCNTs* for Pressure/Touch Sensors

Just like the piezoelectricity, the piezoresistive behavior has also been widely explored to develop pressure or touch sensors, especially to measure the static contact events such as holding an object in one position for long time [11]. The methods exploring piezoresistive behavior, often involve sensors made by mixing the conductive fillers (e.g. CNTs, metals, etc.) with polymeric materials such as PDMS. The composites so obtained are used to measure a single contact event upon change in resistance of the bulk nanocomposite layer, as shown in Fig. 1 (b) [1, 29-31]. The combination of *P(VDF-TrFE)* and MWCNTs, presented here, allows measuring the dynamic as well as static pressures, as presence of *P(VDF-TrFE)* helps in measuring the dynamic component of the stimuli and MWCNTs allows measurement of the static components of the stimuli [9, 10, 32-35]. Due to the high aspect ratio of MWCNTs

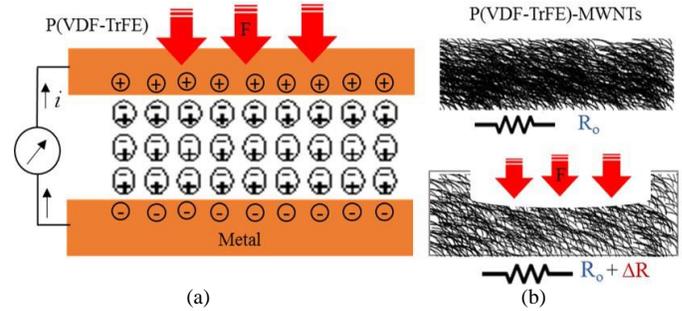


Fig. 1 (a). Mechanism of piezoelectric sensor operation. The current flows when two metallic terminals of piezoelectric material are subjected to external compressive force. (b). Change in bulk resistance of piezoresistive nanocomposite before and after applying external compressive force.

as compared to metallic conductive fillers, the MWCNTs in

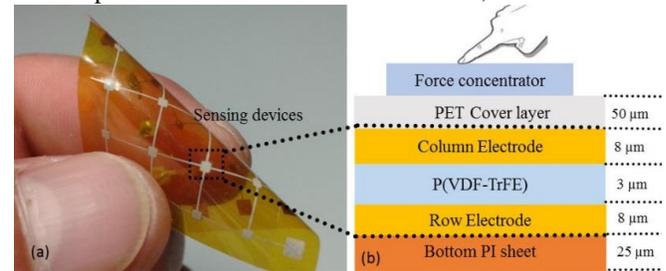


Fig. 2 (a). Optical micrograph of the whole package of 4x4 sensor array, (b). Cross sectional view of the internal structure.

*P(VDF-TrFE)* also results in lower percolation threshold, which makes it easy print the solution as it has medium viscosity.

### C. Technology for Large Area Sensors

A number of fabrication technologies have been reported in literature for *P(VDF-TrFE)* based sensors. These include spin coating, thermally drawn functional fibers, micro-machined mold transfer, single and multiplayer inkjet printers and electrospinning processes [14, 15, 34, 36, 37]. The issues with most frequently used techniques such as spin coating and inkjet printing are the poor processing speed and overlay registration accuracy, especially in multilayer structures. The spin coating route for patterning of *P(VDF-TrFE)* also requires additional photolithography steps, which add to the cost of fabrication. Screen-printing is the preferred alternative in this regard. Having practiced in the industry for last 50 years, screen-printing is a mature technology with stable processing conditions. Further, the materials for optimum physical and electrical characteristics have already been developed [18, 38, 39]. It has been used to realize multilayer high-density flexible electronic circuits with embedded passive and optical devices, large area humidity and temperature sensors [16, 19, 40]. Screen printing is attractive for capacitive structures of *P(VDF-TrFE)*, as there are no moving tools and parts, which means there are lesser issues to deal with related to the sensor design, fabrication, interconnects and packaging [17, 19, 35, 41]. The major research on employing screen-printing for piezosensors has been about patterning of electrodes and sensing area on commercially available PET sheets. However, not much has

been reported about P(VDF-TrFE) patterning and fully printed sensors on ultrathin plastic and flexible substrates [42].

## II. EXPERIMENTS

### A. Basic structure of the sensor array

In this work, we report the sensors based on P(VDF-TrFE) and P(VDF-TrFE)-MWCNTs nanocomposites. The silver (Ag) (DuPont-5028) paste has been used for the conductive plates and interconnects, and the UV-curable dielectric paste (DuPont-5018) is used for realizing the force concentrators. The Ag and dielectric pastes are used as received from the supplier, as the properties of these materials are already adjusted for use with screen-printing technology. A sensor module and its structure are shown in Fig 2 (a)-(b).

### B. Preparation of P(VDF-TrFE) solution and P(VDF-TrFE)-MWCNTs nanocomposites

The MWCNTs used in nanocomposite are supplied by Sigma-Aldrich, USA, with a purity >95%, outside diameter 6-9 nm and length of 5  $\mu\text{m}$ . In this work, the polymer matrix used in the nanocomposite is P(VDF-TrFE) (Piezotech S.A.S, France). The 15 wt.% P(VDF-TrFE) solution was obtained by dissolving P(VDF-TrFE) pellets (70/30% mole composition) in methylethylketone (MEK) solvent. The solution was stirred for 12 hours at 100°C. Then MWCNTs were ultrasonically dispersed in the solution for about an hour. The power and frequency of sonication were 70 W and 42 kHz respectively. The nanocomposites with 1, 2 and 3 wt. % of MWCNTs were prepared.

### C. Screen Printing of P(VDF-TrFE)

For the parallel plate capacitive structures shown in Fig. 2 (a)-(b), the silver (Ag) paste was used for the top and bottom electrodes. The viscosity of the paste was in the range of 15-30 Pa.s. The conductive tracks for bottom electrodes are divided into 4 modules of 4×4 array each. The sensing or active area is 1×1 mm<sup>2</sup>, connected through 100  $\mu\text{m}$  wide printed interconnects. The distance between two adjacent sensors is 5.6 mm. The 2×2 mm<sup>2</sup> pads for the readout signals are coupled with printed bottom electrodes. The dimensions of the screen mask are shown in Fig. 3. After first printing step the samples were sintered at 120°C for an hour. A separate stencil mask with 3×3 mm<sup>2</sup> opening area, overlapping the bottom electrode was then used for printing of P(VDF-TrFE). Both stencil masks are designed to maintain the overlay registration accuracy. The critical parameters for screen-printing parameters such as squeegee height, pressure on the stencil, speed, snap-off and offset for the screen stage were all monitored to obtain efficient printing. Deposited layers were sintered in vacuum at 140°C for about 4 hours to completely remove the solvents and enhance recrystallization of P(VDF-TrFE). The top electrodes were then patterned on a separate PET substrate using the stencil mask, which was employed for the lower electrodes. However, the stencil was rotated by 90° with respect to lower electrode to obtain sensors in the row-column fashion. The schemes of the stencils used for printing sensor structures are shown in Fig. 3 (a)-(c).

### D. Printing of MWCNTs/P(VDF-TrFE)

For simplicity, and to limit the fabrication costs, the

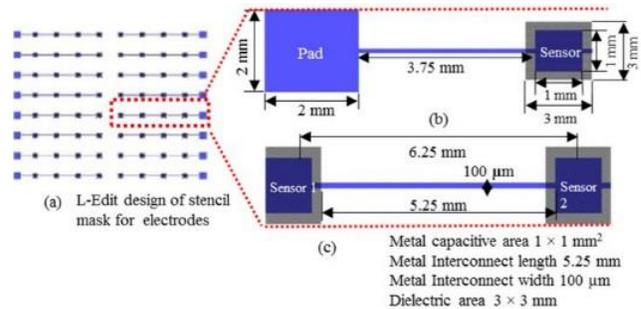


Fig. 3 (a). Schematic of the stencil mask for screen printer. (b). Dimension of pads and active sensitive area (c) Dimension of individual sensor and distance between consecutive sensors.

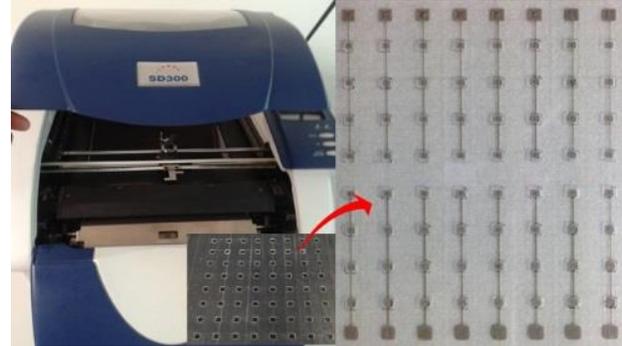


Fig. 4. 3D-Printer with developed shadow masks for nanocomposite.

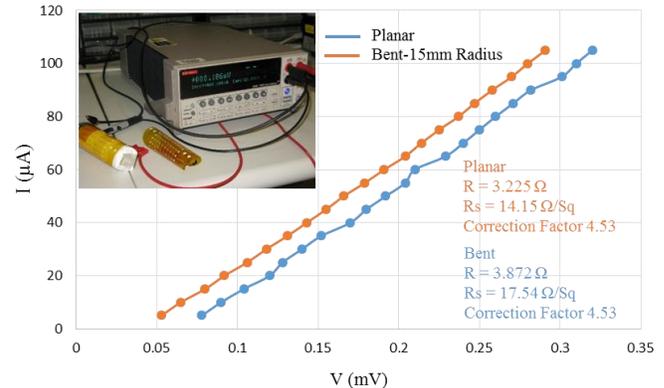


Fig. 5. Sheet resistivity in planar and bent mode (radius 25 mm) of substrate [3].

nanocomposites of P(VDF-TrFE)-MWCNTs were deposited on the bottom electrodes by manual screen-printing. For this purpose, a hard mask was designed and prepared with a 3D printer (SD300, Solidimension) shown in Fig. 4. The dimension of via openings is 3×3 mm<sup>2</sup> and the thickness of shadow mask is 0.5 mm. The flexible substrate was mounted on a rigid planar carrier wafer, which was then placed on a stage equipped with a vacuum chuck. During printing, the wafer and the shadow mask were fixed over the stage, and to each other as well through the vacuum chuck. The squeegee was controlled by hand while moving forward slowly. After one run of printing the rest of the materials were collected and mask was carefully removed from the wafer. The printed wafer was then sintered in an oven at 140°C for 2.5 hours. Fig. 4 shows the image of the shadow mask prepared with 3D printer to be used on top of pre-printed silver electrodes and interconnect lines.

#### IV. RESULTS AND DISCUSSIONS

The screen-printed conductive patterns were characterized to determine various physical and electrical parameters for a reliable printed sensor. Screen-printing deposits thick layers as compared to other patterning/printing tools. This has strong bearing on the physical properties of the printed layers. The prime characteristics needed for investigation of printed patterns include thickness measurements, adhesion to the substrate under different conditions of humidity and temperatures, print efficiency and sheet resistance of the printed layers. The adhesion of subsequent materials on the sintered Ag lines was also checked under different orientations i.e. in planar and bent mode of 25 mm radius. The C-V measurements of the piezoelectric materials were performed before and after polarization with planar and bent orientations. Finally the response of the piezoelectric sensors was checked at different frequencies and applied forces while piezoresistive sensors were subjected to different compressive forces. These characterization techniques and the results are discussed in following sub-sections.

##### A. Sheet Resistance of conductive patterns

The sheet resistance of conductive patterns was measured in planar and bent mode to verify any change in the conductivity as a result of bending. For this purpose, a four-point collinear probe setup was developed with high impedance Keithley 7410 voltmeter for current and voltage analysis. Resistance was measured for one complete row of the printed electrodes. In the collinear configuration, the outer two probes placed at the center of printed plates were used to source the current while the two probes placed on the central points of the inner two plates were used to determine the voltage drop across the whole line. The sheet resistance value given by the supplier for the printed silver paste is about  $12 \Omega/\text{sq}$ , for a  $25 \mu\text{m}$  thick layer. The sheet resistance measured in our samples ( $\sim 8 \mu\text{m}$  thick layer), as shown in Fig. 5, is  $14.15 \Omega/\text{sq}$  in the planar mode. This is within the range of expected sheet resistivities of silver paste after sintering. The sheet resistivities of the same printed lines were checked at different orientations and substrate bending. In the bending mode, with radius of  $\sim 25 \text{ mm}$ , the sheet resistivities were observed to be  $\sim 17.54 \Omega/\text{sq}$ , which is little higher than the corresponding value in planar mode. This could be due to the variation in layer thickness and possibly because of microcracks that may have appeared during the bending. Nonetheless, the resistivities in both the planar and bending mode are acceptable for our application in the piezoelectric sensors.

##### B. Profilometry and optical microscopic analysis

After complete sintering in a vacuum environment, the samples were analyzed with mechanical profilometer and microscope to measure the thickness of conductive patterns and to analyze the deposited P(VDF-TrFE) layers. Fig 6 (a) - (b) show the profilometer and SEM image of the silver and porous structure of P(VDF-TrFE) layer respectively. The porous structure observed through SEM was also confirmed by printing of Ag paste on top of P(VDF-TrFE), as this resulted in short circuiting after sintering. This is one of the reasons for printing top electrode on a separate PET substrate and not directly on the P(VDF-TrFE).

TABLE I  
ADHESION-LOSS TEST OF THE PRINTED LAYERS.

Samples	Temperature, °C	Humidity, gm/m <sup>3</sup>	Observation
Interconnect Lines	25	16	No Detachment
	40	40	2 Lines (12% of the total length) detached.
	80	80	3 Lines (18% of the total length) detached
Dielectric (Force Concentrators)	25	16	No detachment
	40	40	No detachment
	80	80	No detachment
P(VDF-TrFE) and P(VDF-TrFE)/MWCNTs	25	16	No detachment
	40	40	Detached completely
	80	80	Detached completely

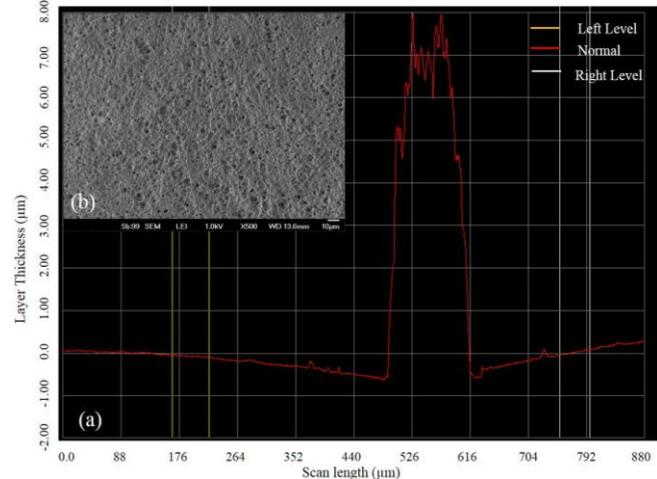


Fig. 6. (a). Thickness measure of the Printed silver (Ag) layer, (b). SEM image of P(VDF-TrFE) layer.

Mechanical profilometer is used to check the thickness of both conductive patterns and the P(VDF-TrFE) layer. Printed metal plates and interconnects were observed at different positions and the thickness was found to be  $\sim 8 \mu\text{m}$ . Thickness of the printed P(VDF-TrFE) layer is found to be  $\sim 3 \mu\text{m}$ . The thickness of the P(VDF-TrFE) layer can be controlled by either changing the material proportions or by choosing different screen printing parameters. Due to high vaporization rate the MEK, used as solvent for P(VDF-TrFE), also affects the uniformity and thickness of sensor layer. In addition, properties of the residual solution collected back after the screen-printing, is not similar to the initial properties of the solution. Due to evaporation of the solvent rapidly, complete collection of the residual solution is also one of the main hindrances in this approach. As a result, a major proportion of the solution is wasted in re-collection process and a dried layer of P(VDF-TrFE) is left on the screen mask right after printing, which is hard to clean. The obstacle of high evaporation rate of the solvent can be overcome by investigating an appropriate

screen-printing compatible solvent having low vaporization rate at room temperature. This will allow maintaining uniformity of various layers between the two printed metal plates with 100% overlay registration accuracy.

In contrast to the P(VDF-TrFE) printing explained above, the manual screen-printing of nanocomposite layers of P(VDF-TrFE)/MWNTs results in higher thicknesses. The MWNTs in the polymer matrix lead to increased viscosity of the solution, and hence contribute to the increased thickness of the printed layers. To print highly viscous solutions at minimized thicknesses, one solution is to reduce the thickness of the shadow mask, that can be tuned by changing the designs in the 3D printer [43]. The thickness varies with increased ratio of MWNTs in P(VDF-TrFE). The optimum thicknesses achieved with 1-4 wt. % ranged from 10 -25  $\mu\text{m}$ . Due to the manual printing of these nanocomposites materials, reproducibility of the process parameters is not as accurate as printing through automated screen printer. Uniformity of the manual printing is also hard to control as the results are highly dependent on the process parameters like squeegee pressure, speed and snap-off of the screen from the stage holding substrate on top of it.

### C. Humidity test of the printed layers

The environmental conditions such as temperature and humidity have a direct bearing on the performance and reliability of sensors. In this context, the reliability of the adhesion of printed layers to polymeric substrates under varying environmental conditions is critical. Being pyroelectric, P(VDF-TrFE) is also sensitive to temperature changes. However, this is not covered here as it is out of the scope of present research. The adhesion of printed layers, including conductive interconnect lines, P(VDF-TrFE), P(VDF-TrFE)/MWNTs nanocomposites, and the dielectric layers used for force concentrated structures, were evaluated under different temperature and humidity conditions.

Simple peel-off test was performed with a scotch tape on the printed layers and detaching of some of these patterns from substrates was observed. These tests were performed under three different temperature and humidity conditions. Initially, the samples were evaluated under room temperature and humidity of 16  $\text{g}/\text{m}^3$ . For rest of the two tests the samples were kept in a humidity chamber at absolute humidity of 40  $\text{g}/\text{m}^3$  and 80  $\text{g}/\text{m}^3$ , while temperature was also raised at the same rate in two steps from 40  $^\circ\text{C}$  to 80  $^\circ\text{C}$ . The samples were kept in humidity chamber for 15 minutes and then taken out for adhesion test. Scotch tape was applied on the samples immediately after withdrawal from the humidity chamber and the same procedure was followed for second and third set of experiments. At room temperature and 16  $\text{g}/\text{m}^3$  of humidity, no pickups of interconnect wires or a force concentrator structure was observed. Only two interconnect lines at the center (12% of the total interconnects length) got detached at 40 $^\circ\text{C}$  and absolute humidity of 40  $\text{g}/\text{cm}^3$ . For 80 $^\circ\text{C}$  and 80  $\text{g}/\text{cm}^3$  of the temperature and humidity, three interconnect line of (18% of the total interconnects) was observed to be detached. In case of transducer layer a strong adhesion to the bottom electrodes as well as with polymeric substrate, was observed at room temperature. Dimensions of P(VDF-TrFE) layers used in

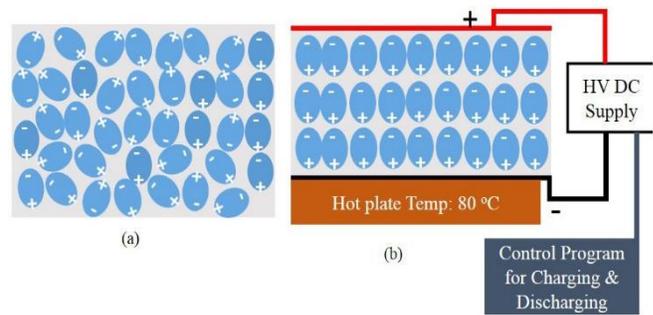


Fig. 7. P(VDF-TrFE) layers before and after poling, (a) Schematic of semi-crystalline polymer with random dipoles, (b) Experimental setup for poling after which dipoles are aligned in parallel.

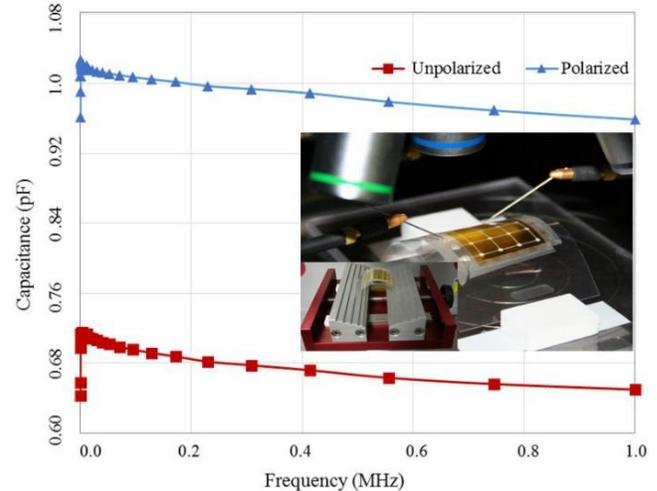


Fig. 8. Capacitance versus frequency response of printed PVDF-TrFE

these experiments are  $3 \times 3 \text{ mm}^2$ , which completely covers the  $1 \times 1 \text{ mm}^2$  metal (Ag) plate and also comes in contact with the flexible substrate on the periphery of the active areas. However, at the raised humidity and temperature conditions, the P(VDF-TrFE) and nanocomposites got detached from the metal layers and substrate from all areas where they were screen printed. These observations are summarized in Table I.

The physical and mechanical performance of the sensors is also important as they are to be mounted on an electronic skin for robotics. In this application the skin measure the contact stimulus and provide feedback to robots. The samples were tested under two different orientations, first on a planar surface and then by wrapping them around a cylinder of 15 mm radius. Investigations of the physical properties and the results obtained at varying conditions of temperature and humidity suggest that an encapsulation layer on top of the sensors is necessary to avoid the humidity related issues. One of the readily available solutions is to use PET substrate, which in our case also contains the top electrodes and force concentrator structures.

### D. Polarization

P(VDF-TrFE) is a semi crystalline polymer and polarization or poling of the randomly oriented dipoles is needed to orient them along a specific direction and to enhance the piezoelectric response. A number of techniques have been explored for poling [25], including corona poling and thermal poling. In present case, we used thermal poling as it results in uniform dipole orientation. The screen printed P(VDF-TrFE) samples

were polarized by applying a high voltage ( $\sim 60$  V/ $\mu\text{m}$ ) across the polymer layer at elevated temperature of  $\sim 80$  °C, as shown in Fig. 7 [44]. The samples were put on a hot plate at 80 °C and then the voltage was applied across the metal layers on the pads as shown in Fig. 7. Poling was performed only for the sensors having P(VDF-TrFE). For  $\sim 3$   $\mu\text{m}$  thick P(VDF-TrFE) the maximum potential of 180 volts was applied in 6 incremental steps of 30 volts each. Electric field was applied for 10 minutes at each incremental step. Between two voltage application steps, the metal electrodes on two sides of P(VDF-TrFE) samples were short circuited for about 5 minutes to neutralize extra charges and mitigate the electric breakdown.

#### E. Capacitance-Voltage (C-V) and Piezoelectricity Measurements:

The C-V measurements at varying frequencies were made before and after the polarization to verify the effect of polarization. The software controlled Agilent 4284A precision LCR meter was used for this purpose. The frequency used for experiment ranged between 100Hz and 1MHz and peak oscillating voltage was kept at 10mV with hold time of 1 sec. The frequency was increased in a total of 30 steps. The capacitance values at different frequencies are given in Fig. 8. We recorded an increase in capacitance of approximately 26 pF for screen-printed sensors after polarization. This difference is consistent among various devices - both polarized and nonpolarized. In general, the frequency response of the devices aligns with that reported in the literature for flexible pressure sensors.

The piezoelectric properties of a device were also investigated at different frequencies and applied forces. The scheme of the setup used for this purpose is similar to the one described in [45]. The set up, shown in Fig. 9 (a & b), consists of force sensor, vibrator, charge amplifier, data acquisition and signal conditioning. The sensor was tested by applying forces in 0.5 - 3.0 N range applied forces at 10Hz, 50Hz and 200Hz frequencies. The force concentrator structures, developed by using UV curable (DuPont 5018) dielectric ink on the backside of the substrate having top electrodes, were used to intensify the applied force on the sensors. These force concentrators cover the whole effective area of the sensor and are aligned to load cell tip with a xyz positioning stage. At frequencies lower than 50 Hz, the sensor's response was recorded as 0.05V/N for dynamic force applied in normal direction. For frequencies greater than 100 Hz, the response increases approximately in linear fashion as shown in Fig 10. For instance, at the constant force of 3N there is an increase in the voltage of about 0.07 V at 200 Hz and 0.02 V at 100 Hz, compared to the response of the sensor at similar applied force at 50 Hz. The changes in response values of screen-printed samples may be due to variations in the thicknesses and uniformity of the layers.

#### F. Resistance measurement of P(VDF-TrFE)-MWCNTs

The motivation for using the nanocomposites of P(VDF-TrFE)-MWCNTs is to tune the resistance of the polymer matrix by adding conductive fillers. The change in resistance is due to variations in the conduction paths generated by networks of MWCNTs. The MWCNTs dispersed uniformly within the matrix contribute to the bulk conductivity. The deformation of material would break the conductive paths in the matrix and

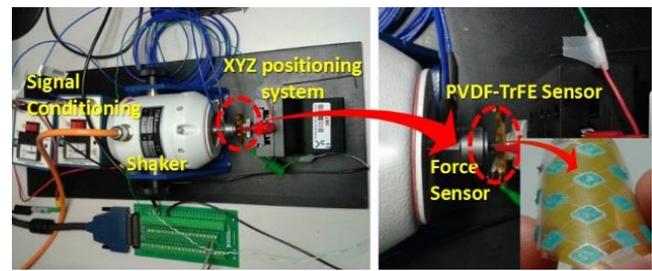


Fig. 9. (a) Shaker setup for application of dynamic force on the pressure sensor. (b). Final developed sensor module subjected to dynamic force.

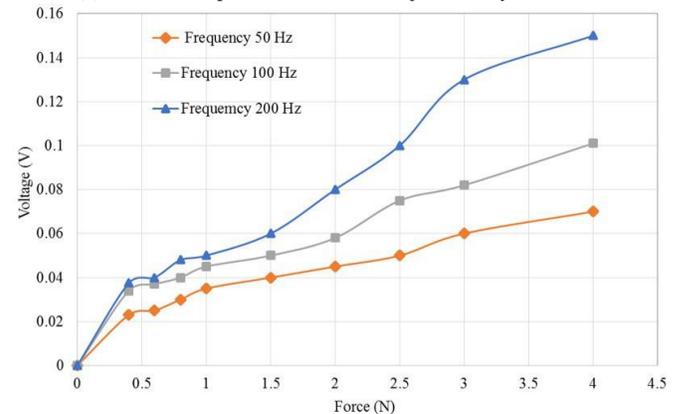


Fig. 10. Piezoelectric response of screen printed P(VDF-TrFE) sensors against different applied normal forces at various frequencies.

lead to an instantaneous change in the bulk resistance. The initial value of bulk resistance is adjusted by subjecting the sensors to normal compressive forces. In doing so the orientation of established conductive network of MWCNTs is significantly changed. These changes are also assisted by the tunneling effect, which occurs when the conductive entities are close to each other.

Elastomeric materials are more suitable for the percolation mechanism where the elastic deformation causes change in the bulk resistance of the metallic nanocomposite. This change in resistance upon application of a compressive force is exploited for the purpose of a pressure sensor. P(VDF-TrFE) is not an elastomeric material, but a small operating window for pressure sensor can still be obtained. P(VDF-TrFE) possesses properties similar to amorphous semiconductors, where dipoles are randomly distributed within the bulk, increasing the ratio of MWCNTs results in sharp increase of the conductivity of the P(VDF-TrFE). To find out the optimum ratio of MWCNTs in P(VDF-TrFE) for printing, various mixtures of nanocomposite were prepared with different concentrations. The samples were characterized after printing and curing steps described in section III. By testing the resistance of the samples without applying any force, it is found that by increasing the ratios  $>2$  wt. % of MWCNTs, the layers become fully conductive. Samples with 2 wt. % are checked randomly and the average value of resistance found is about  $\sim 40$  k $\Omega$ . Compared to 2 wt% CNTs samples, the 1 wt. % CNTs showed very high resistance  $>10\text{M}\Omega$ . Lack of continuous conductive networks and agglomeration of MWCNTs at random spots hinders the change in resistance on application of compressive force for 1wt. %.

Fig. 11 (a) shows the sensors developed by patterning nanocomposite of P(VDF-TrFE)/MWCNTs [46].

The low percolation threshold i.e.  $\sim 2$  wt. % is an indication for the using these nanocomposites applications beyond pressure sensors. With low mixing ratios the solution viscosity can be kept in acceptable ranges to allow screen printing and simplified patterning of a variety of structures. Besides pressure sensors, the prototype of conductive interconnect lines are also printed as shown in Fig. 11 (b) [46]. The conductive polymeric interconnects are in demand for stretchable electronics. For this purpose, low concentrations provide an opportunity to reduce agglomeration of the MWCNTs within the bulk material, which is one of the obstacles for using them for sensors and interconnects.

Further investigation is required to optimize the percolation threshold to increase the operating window of the sensors. Printing pressure sensors on flexible substrates and connecting them through the interconnects developed from nanocomposites of P(VDF-TrFE) will lead the technology beyond flexible or foldable electronics towards stretchable electronics such as electron skin.

## V. CONCLUSION

The large area pressure sensor arrays presented in this work are obtained by sandwiching P(VDF-TrFE) and P(VDF-TrFE)/MWCNTs nanocomposites between two patterned silver electrodes. A total of 64 sensors have been fabricated in one flow by screen-printing. Two screen-printing approaches have been adopted and analyzed for optimizing the parameters, on the basis of ease of processing, robustness, time saving, material efficiency and compatibility of layer by layer structures. Besides using standard screen mask, a manual screen printing is presented for deposition of nanocomposites of MWCNTs/P(VDF-TrFE). Screen-printing appears to be attractive for multilayered printed electronic. Adhesion-loss tests performed at different humidity and temperatures for P(VDF-TrFE) show poor adhesion to plastic substrates. Encapsulant in the form of PET substrate comprising top electrode and force concentrator structures are used for covering P(VDF-TrFE) in order to avoid short circuit. In addition, a piezoresistive material, nanocomposite of P(VDF-TrFE)/MWCNTs is also investigated in this research. It is patterned using a manual screen-printing technique through a shadow mask developed by a 3D printer. This is convenient method as, in comparison with the standard screen meshes for deposition of a nanocomposite, it guarantees the uniform dispersion of conductive nanofillers within the matrix. Change in resistance is recorded for different weight percentages of MWCNTs in P(VDF-TrFE) matrix indicates that the nanocomposites with ratios greater than 2 wt. % become completely conductive. This result is promising for development of pressure sensors using lower percolation threshold nanocomposites. The successful patterning of P(VDF-TrFE) and the nanocomposites in single step with uniform thickness show that the potential for the method in applications beyond electronic skin. Further investigation of compatible solvents for P(VDF-TrFE) with low evaporation rate and well matching with the viscosity range of the screen-printing will be explored in the future.

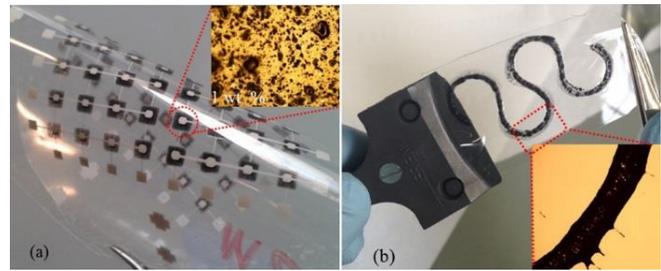


Fig. 11. (a). Printed sensors based on P(VDF-TrFE)/MWCNTs on PET substrate and optical image of 1 wt.% nanocomposite layer. (b) Interconnect lines of P(VDF-TrFE)-MWCNTs on flexible substrate.

## References

- [1] S. Khan, R. S. Dahiya, and L. Lorenzelli, "Bendable Piezoresistive Sensors by Screen Printing MWCNT/PDMS Composites on Flexible Substrates," in *10th Int. Conf. on Ph.D Res. in Microelectr. and Electr.*, Grenoble, France, 2014.
- [2] R. S. Dahiya, P. Mittendorfer, M. Valle, G. Cheng, and V. Lumelsky, "Directions Towards Effective Utilization of Tactile Skin -- A Review," *IEEE Sensors J.*, vol. 13, pp. 4121-4138, 2013.
- [3] R. S. Dahiya and M. Valle, *Robotic Tactile Sensing - Technologies and System*. Dordrecht: Springer, 2013.
- [4] R. S. Dahiya, G. Metta, M. Valle, and G. Sandini, "Tactile Sensing - From Humans to Humanoids," *IEEE Trans. Robot.*, vol. 26, pp. 1-20, 2010.
- [5] Ravinder Dahiya, William Taube Navaraj, Saleem Khan, and E. O. Polat. (2015, Developing Electronic Skin with the Sense of Touch. *frontline Technology 31(6)*.
- [6] N. Yogeswaran, S. Tinku, S. Khan, L. Lorenzelli, V. Vinciguerra, and R. Dahiya, "Stretchable Resistive Pressure Sensor based on CNT-PDMS Nanocomposites," presented at the 11th Int. Conf. on Ph.D Res. in Microelectr. and Electr., Glasgow, UK, 2015.
- [7] S. Khan, R. S. Dahiya, and L. Lorenzelli, "Screen Printed Flexible Pressure Sensors Skin," in *ASMC 2014 - The 25th Annual Advanced Semiconductor Manufacturing Conference*, NY, USA, 2014, pp. 219-224.
- [8] A. B. da Silva, J. Marini, G. Gelves, U. Sundararaj, R. Gregório, and R. E. Bretas, "Synergic effect in electrical conductivity using a combination of two fillers in PVDF hybrids composites," *European Polymer Journal*, vol. 49, pp. 3318-3327, 2013.
- [9] L. Wu, W. Yuan, N. Hu, Z. Wang, C. Chen, J. Qiu, *et al.*, "Improved piezoelectricity of PVDF-HFP/carbon black composite films," *Journal of Physics D: Applied Physics*, vol. 47, p. 135302, 2014.
- [10] E. El Shafee, M. El Gamal, and M. Isa, "Electrical properties of multi walled carbon nanotubes/poly (vinylidene fluoride/trifluoroethylene) nanocomposites," *Journal of Polymer Research*, vol. 19, pp. 1-8, 2012.
- [11] S. Khan, S. Tinku, R. S. Dahiya, and L. Lorenzelli, "Flexible Tactile Sensors using Screen Printed P(VDF-TrFE) and MWCNT/PDMS Composites," *Sensors Journal, IEEE*, vol. 15, pp. 3146-3155, 2015.
- [12] S. Khan, R. Dahiya, and L. Lorenzelli, "Technologies for Printing Sensors and Electronics over Large Flexible Substrates: A Review," *Sensors Journal, IEEE*, vol. 15, pp. 3164-3185, 2015.
- [13] Y. Wang, J. Zheng, G. Ren, P. Zhang, and C. Xu, "A flexible piezoelectric force sensor based on PVDF fabrics," *Smart Materials and Structures*, vol. 20, p. 045009, 2011.
- [14] O. Pabst, J. Perelaer, E. Beckert, U. S. Schubert, R. Eberhardt, and A. Tünnermann, "All inkjet-printed piezoelectric polymer actuators: Characterization and applications for micropumps in lab-on-a-chip systems," *Organic Electronics*, vol. 14, pp. 3423-3429, 2013.
- [15] C. Li, P.-M. Wu, S. Lee, A. Gorton, M. J. Schulz, and C. H. Ahn, "Flexible dome and bump shape piezoelectric tactile sensors using PVDF-TrFE copolymer," *Microelectromechanical Systems, Journal of*, vol. 17, pp. 334-341, 2008.
- [16] W.-Y. Chang, T.-H. Fang, H.-J. Lin, Y.-T. Shen, and Y.-C. Lin, "A large area flexible array sensors using screen printing technology," *Journal of display technology*, vol. 5, pp. 178-183, 2009.

- [17] M. Dietze and M. Es-Souni, "Structural and functional properties of screen-printed PZT–PVDF–TrFE composites," *Sensors and Actuators A: Physical*, vol. 143, pp. 329-334, 2008.
- [18] D. Numakura, "Advanced Screen Printing" Practical Approaches for Printable & Flexible Electronics," in *Microsystems, Packaging, Assembly & Circuits Technology Conference, 2008. IMPACT 2008. 3rd International*, 2008, pp. 205-208.
- [19] C. Shi, X. Shan, G. Tarapata, R. Jachowicz, J. Weremczuk, and H. Hui, "Fabrication of wireless sensors on flexible film using screen printing and via filling," *Microsystem technologies*, vol. 17, pp. 661-667, 2011.
- [20] J. S. Dodds, F. N. Meyers, and K. J. Loh, "Piezoelectric characterization of PVDF-TrFE thin films enhanced with ZnO nanoparticles," *Sensors Journal, IEEE*, vol. 12, pp. 1889-1890, 2012.
- [21] S. Hannah, H. Gleskova, S. Khan, and R. Dahiya, "Response of P(VDF-TrFE) Sensors to Pressure and Temperature," presented at the 11th Int. Conf. on PhD Res. in Microelectr. and Electr., Glasgow, UK., 2015.
- [22] J. Cheng, O. Amft, and P. Lukowicz, "Active capacitive sensing: Exploring a new wearable sensing modality for activity recognition," in *Pervasive Computing*, ed: Springer, 2010, pp. 319-336.
- [23] L. Pinna, R. S. Dahiya, and M. Valle, "SPICE Model for Piezoelectric Bender Generators," in *Electronics, Circuits, and Systems, 2009. ICECS 2009. 16th IEEE International Conference on*, 2009, pp. 587-590.
- [24] C. Costa, L. Rodrigues, V. Sencadas, M. Silva, J. Rocha, and S. Lanceros-Méndez, "Effect of degree of porosity on the properties of poly (vinylidene fluoride–trifluoroethylene) for Li-ion battery separators," *Journal of Membrane Science*, vol. 407, pp. 193-201, 2012.
- [25] R. S. Dahiya, M. Valle, G. Metta, L. Lorenzelli, and S. Pedrotti, "Deposition, processing and characterization of P(VDF-TrFE) thin films for sensing applications," in *9th IEEE Sensors Conf.*, Lecce, Italy, 2008, pp. 490-493.
- [26] Y. Jia, X. Chen, Q. Ni, L. Li, and C. Ju, "Dependence of the Impact Response of Polyvinylidene Fluoride Sensors on Their Supporting Materials' Elasticity," *Sensors*, vol. 13, pp. 8669-8678, 2013.
- [27] A. Adami, R. S. Dahiya, C. Collini, D. Cattin, and L. Lorenzelli, "POSFET touch sensor with CMOS integrated signal conditioning electronics," *Sensors and Actuators - A*, vol. 188, pp. 75-81, 2012.
- [28] R. S. Dahiya, A. Adami, C. Collini, and L. Lorenzelli, "POSFET Tactile Sensing Arrays using CMOS Technology," *Sens. & Actuat. - A*, vol. 202, pp. 226-232, 2013.
- [29] C.-X. Liu and J.-W. Choi, "Improved dispersion of carbon nanotubes in polymers at high Concentrations," *Nanomatr.*, pp. 329-347, 2012.
- [30] H. S. Nalwa, *Ferroelectric Polymers - Chemistry, Physics and Applications*. New York: Marcel Dekker Inc, 1995.
- [31] C. L. Wu, H. C. Lin, J. S. Hsu, M. C. Yip, and W. Fang, "Static and dynamic mechanical properties of polydimethylsiloxane/carbon nanotube nanocomposites," *Thin Solid Films*, vol. 517, pp. 4895-4901, 2009.
- [32] S. A. Carabineiro, M. F. Pereira, J. N. Pereira, C. Caparros, V. Sencadas, and S. Lanceros-Mendez, "Effect of the carbon nanotube surface characteristics on the conductivity and dielectric constant of carbon nanotube/poly (vinylidene fluoride) composites," *Nanoscale research letters*, vol. 6, pp. 1-5, 2011.
- [33] S.-h. Hwang, D. S. Bang, K. H. Yoon, and Y.-B. Park, *Smart materials and structures based on carbon nanotube composites*: INTECH Open Access Publisher, 2011.
- [34] Z. Liu, C. Pan, L. Lin, and H. Lai, "Piezoelectric properties of PVDF/MWCNT nanofiber using near-field electrospinning," *Sensors and Actuators A: Physical*, vol. 193, pp. 13-24, 2013.
- [35] W. Dang, S. Khan, L. Lorenzelli, V. Vinciguerra, and R. Dahiya, "Stretchable Interconnects using Screen Printed Nanocomposites of MWCNTs with PDMS and P(VDF-TrFE)," presented at the 11th Int. Conf. on PhD Res. in Microelectr. and Electr., Glasgow, UK., 2015.
- [36] V. Cardoso, G. Minas, C. M. Costa, C. Tavares, and S. Lanceros-Mendez, "Micro and nanofilms of poly (vinylidene fluoride) with controlled thickness, morphology and electroactive crystalline phase for sensor and actuator applications," *Smart Materials and Structures*, vol. 20, p. 087002, 2011.
- [37] X. He and K. Yao, "Crystallization mechanism and piezoelectric properties of solution-derived ferroelectric poly (vinylidene fluoride) thin films," *Applied physics letters*, vol. 89, p. 112909, 2006.
- [38] G. E. Jabbour, R. Radspinner, and N. Peyghambarian, "Screen printing for the fabrication of organic light-emitting devices," *Selected Topics in Quantum Electronics, IEEE Journal of*, vol. 7, pp. 769-773, 2001.
- [39] I. E. H. El Jazairi, T. Trigaud, and J.-P. Moliton, "OTFT with silk screen printed Drain and Source," *Micro and Nanosystems*, vol. 1, pp. 46-49, 2009.
- [40] W.-Y. Chang, T.-H. Fang, S.-H. Yeh, and Y.-C. Lin, "Flexible electronics sensors for tactile multi-touching," *Sensors*, vol. 9, pp. 1188-1203, 2009.
- [41] K. Arshak, D. Morris, A. Arshak, O. Korostynska, and K. Kaneswaran, "Investigation into the pressure sensing properties of PVDF and PVB thick film capacitors," in *Electronics Technology, 2006. ISSSE'06. 29th International Spring Seminar on*, 2006, pp. 334-339.
- [42] M. Zirkl, G. Scheipl, B. Stadlober, A. Haase, L. Kuna, J. Magnien, et al., "Fully printed, flexible, large area organic optothermal sensors for human-machine-interfaces," *Procedia Engineering*, vol. 5, pp. 725-729, 2010.
- [43] S. Khan, W. Dang, L. Lorenzelli, and R. Dahiya, "Printing of high concentration nanocomposites (MWNTs/PDMS) using 3D-printed shadow masks," in *AISEM Annual Conference, 2015 XVIII*, 2015, pp. 1-4.
- [44] M. V. R. S. Dahiya, G. Metta, L. Lorenzelli, and S. Pedrotti, "Deposition, processing and characterization of P(VDF-TrFE) thin films for sensing applications," presented at the IEEE Sensors, The 9th IEEE Conference on Sensors, Lecce, Italy, 2008.
- [45] R. S. Dahiya, G. Metta, M. Valle, A. Adami, and L. Lorenzelli, "Piezoelectric oxide semiconductor field effect transistor touch sensing devices," *Applied Physics Letters*, vol. 95, p. 034105, 2009.
- [46] N. Yogeswaran, S. Khan, W. Dang, E. O. Polat, L. Lorenzelli, V. Vinciguerra, et al., "Tuning Electrical Conductivity of CNT-PDMS Nanocomposites for Flexible Electronic Applications," in *15th International Conference on Nanotechnology, IEEE Nano*, Rome, Italy., 2015, p. In Press.