IJASRM

International Journal of Advanced Scientific Research and Management, Volume 3 Issue 12, Dec 2018

www.ijasrm.com

ISSN 2455-6378

Self-potentially enhanced electrode based hybrid thin film sensor for Delicate Bio-medical Applications

Fazle Kibria[1*] and Sankar Narayan Patra[1]

[1]Dept. of Instrumentation Science, Jadavpur University, Kolkata 700032, India

Abstract

Self potentially enhanced electrode based hybrid thin film sensor was fabricated with a completely simple and homemade technique where PDMS is the agent for electro-responsive means with aluminum foil as substrate and gold deposition were made on the PDMS. Deposited gold is co-operating to attract the molecular –CH2 /−SiO dipoles of the polymer causing charge double layer formation at bio contact region which introduce electro-responsivity without significant mechanical stressing. High natural potential difference between gold (Au) and aluminum (Al) was utilized to create hybrid electrode as well as enhanced sensitivity of the fabricated sensor to sharp pick up of delicate bio-medical signals like bio electric, bio acoustic and bio impedance. The sensor is capable of sensing effects from a very tiny change of physiological stress such as breathing, heart sounds, blood flow, intercostals movements and muscle tremor. The generated output can be viewed and analyses in a wide scale for the design of sensitive, self-powered portable devices.

Keywords:*Hybrid electrode, PDMS film, Potential double layer, Polymer thin film, Gold-PDMS film, Electro-responsive film.*

1. Introduction

Latest trend of research and development in science and engineering is portability which relies with smallest in size. The trend implementing in some novel purpose of sensing, measurements, monitoring or some case analysis in the form of diverse area of bio-medical applications specially as a portable devices[1,2,3].Significant development of micro fluidic small size device, notable advancement of nano fabrication technique and quantum concept of dimensionless device fabrication evidently influence the progress of thin film based sensor fabrication[4]. A number of polymer thin film based piezoelectric materials have already been used in medical applications, such as self-powered cardiac pacemaker enabled by flexible single crystalline lead magnesium niobate with lead titanate or PMN-PT [(1-x)Pb(Mg1/3Nb2/3)O3−xPbTiO3] piezoelectric energy harvester which scavenge inexhaustible bio-mechanical energy such as cardiac motion, muscle contraction/relaxation, blood circulation and convert it to electrical energy[5]. Polyvinylidene Fluoride (PVDF)film-based physiological sensing belt was successfully utilizing for a complementary respiration and heartbeat monitoring system[6,7,8]. Health care with wellness wear is an integration of bio-sensors that attach to clothes, digital yarns that transmit bio signals and other data, integrated circuits and microprocessors that process those signals, wired and wireless communication, and software applications that process and analyze vital signs obtained from the bio-sensors[9]. Lab on chip (LOC)demonstrated fabrication of large microfiltration membranes and free-standing beam structures in PDMS[10].Also PDMS-gold nano particles composite film-based bio sensor was implemented to detect cardiac Troponin-I(cTnI)[11] which is a specific cardiac marker in patient's blood serum who are suffering from coronary artery disease (CAD) like Myocardial Infarction (MI)[12]. Stato-dynamic sensitivity, size, weight, device flexibility, corrosive property and body compatibility restrict the use of conventional thin film based device realizations. In this perspective, polymer thin film based device fabrication can significantly reduce mass and surface area of the film with enhanced stato-dynamic sensitivity which could help to increase sensor performance to its extreme level. In this fabrication process Polydimethylsiloxane (PDMS) was automatic choice as polymer materials due to its excellent transparency[13], outstanding elasticity[14], good thermal stability within the temperature range from−50◦C to +200◦C and excellent oxidative property[15,16,17]. The polymer

enables some certain advantages such as favorable optical properties which include transparency above 230 nm and very low auto fluorescence over a wide range of wavelengths compared to other plastic chip materials[18,19]. Low inter molecular forces make the polymer very flexible[20] around the O atom in the Siloxane backbone within 135°-180°[21] and chemical inertness[22] making it attractive for a variety of biological and bio-medical applications. Its performance can be enhanced by modifying surface properties in presence of adsorption like protein rich material or in plasma[23,24]. Excitingly it exhibits large spontaneous polarization and electro-responsivity[25,26]. Although, electro-responsive activity cannot be discarded until the polymer layer gets placed within two metallic electrodes and imposed into a stress which aligns the randomly oriented molecular (-CH2/-SiO) dipoles along the electric field direction referred as electrical charge polarization. In this work, high performance self-potentially enhanced electrode based hybrid thin film sensor was fabricated with completely homemade low costfabrication technique. Thefreestanding thin layered sensor was synthesized by forming micro dimensional wafer of PDMS on 10 µm thin aluminum(Al) foil and a gold (Au) layer of dimension 100 nm-300 nm was deposited on PDMS surface. The fundamental idea behind this approach is to distribute the dynamic potential across the region where electric field due to static charge of the immobile ions and the surrounding mobile charges penetrates each other directions of target interest which generates significant potential differences due to charge affinity in both ends. Investigations of electrical sensitivity were recorded for different bio signals as well as some low mechanical stress input. To the best of our knowledge, this is the first report of this kind of electrode based sensor where potential differences can be generated naturally. In addition to check the feasibility and applicability of the fabricated device, we investigated the output for different electrode materials as well as different target objects.

2. Materials and Experimental Methods

2.1. Preparation of Materials

Dow Corning's Sylgard184 elastomer kit was brought for PDMS thin film formation. Two parts of the kit namely base and curing agent were mixed together in a particular ratio (typically at 10:1 (v/v) base: curing agent) and poured the liquid pre-polymer over the master. Stirred the mixture vigorously with a spatula until the curing agent mixed uniformly with master and observed that the mixture werecontained air bubbles.The mixture was kept in a desiccator connected with a vacuum pumpto remove the trapped air bubbles. The liquid PDMS pre-polymer conforms to the shape of the master and replicates the features of the master with high (10's of nm) fidelity. The low surface free energy and elasticity of the polymer allow it to release from master without damaging the master or itself. The entire film formation performed by solution casting process on a clean glass substrates covered with very thin aluminum foil of thickness 0.01 mm and subsequently dried at 90°C for 2 h on a hot plate represent in Figure 1.(e). Finally, free-standing flexible transparent films [Figure 1.(f)]with aluminum foil in one side of the polymer surface were achieved. The details architectural hierarchy including solution preparation and film formation was demonstrated in Figure 1. (a) to (f).

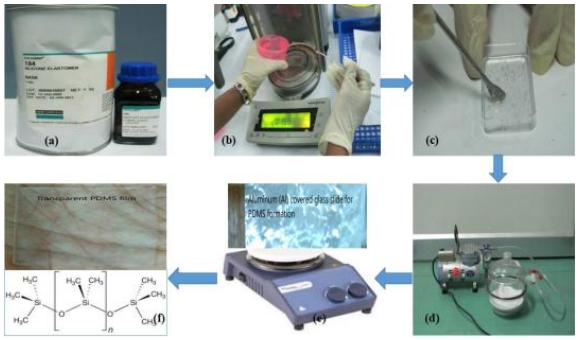

Figure 1. Schematic illustrations of PDMS film formation on aluminum (Al) wrapped glass slide (scale bar, 1 cm). (a) Solution kit with curing agent, (b) Measurement of curing agent (10:1) (c) Mixing of curing agent with PDMS, (d) Desiccating the solution, (e) Heating the slide on hot plate and (f) Free standing transparent PDMS film.

2.2. Fabrication of Self potentially enhanced electrode based hybrid thin film sensor

Fabrication process of the hybrid sensor was schematically illustrated in Figure 2.(a) to (d). In general, analysis of very tiny physiological signal through commercially available thin film based sensor shows no response or low response, to overcome this limitation self potentially enhanced electrode based hybrid thin film sensor was fabricated. Electrospinning is the most conventional latest technique to develop polymer thin film which provides minimum control over film thickness

IJASRM

International Journal of Advanced Scientific Research and Management, Volume 3 Issue 12, Dec 2018

www.ijasrm.com

ISSN 2455-6378

intends less homogeneity on film due to improper accumulation of particles on the surface, and the technique demands some impurity material doping with polymer for film formation. To get rid of from these inconveniences, a simple glass slide based homogeneous self-made technique was adopted. Most significantly the new fabrication technique offers homogeneous thin film formation with PDMS alone. Polymer film obtained from the casting step was cut into pieces of dimension (L x D) 1.0 x 0.15cm2 to fabricate the sensor. As aluminum is already exist on onside of the polymer film which acts as an electrode of the sensor.In other side of the sensor, gold (Au) was deposited by electron sputtering method on the film to perform as a second electrode. The metal surfaces were functioned to collect electrical signals. Narrow gauge thin copper wires connected on both of the electrodes to transmit the output response of the sensor. Here gold (Au) and aluminum (Al) are acting as top and bottom electrodes respectively which offer naturally large electrode potential differences [+1.69-(-1.66) =3.35V] intended to sharp pick up and measure the very small bio-medical signals in a broad view of analysis. Figure 2. (a) represents electrostatic layers of the sensor, Figure 2. (b) and (c) demonstrate physically obtained sensor along with digitized view after gold coating, Figure 2. (d) illustrates internal electrostatic activity of the sensor which actively participated for sensing activity.

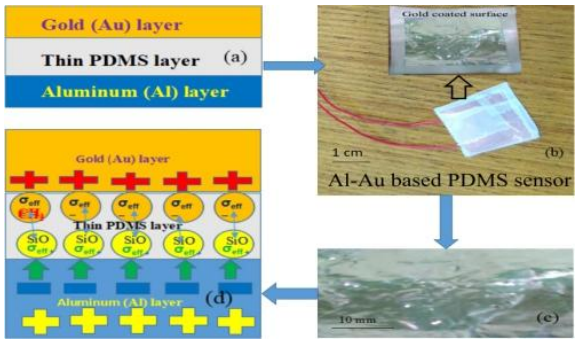

Figure 2. Schematic fabrication progress of the hybrid sensor (a) Three layers, (b) Digital image of the sensor (scale bar, 1 cm), (c) Digital view after gold coating (scale bar, 10 mm) and (d) Internal configuration of the sensor

2.3. Material Characterization

SEM Study:

The surface morphology, particles homogeneity and external atomic arrangement of gold (Au) coated on PDMS ultra-thin electro-responsive film grown over the polymer matrixwere observed under a high resolution scanning electron microscope (Zeiss, FE-SEM). After deposition of high density gold (Au) materials on the low viscous polymer by high vacuum electron sputtering mechanism, surface roughness of the film has been studied. Micrographs were taken at different accelerating voltages of 5KV to 20KV with alternative magnification within 500X to 50KX for the characterization of deposited nano and sub-micron particles. Combined materials with polymer thin film geometry represents slight change in surface crystalline structure of the polymer from its original counterpart interestingly which intends to predict an extra peak for gold (Au) in X-ray diffraction analysis. The measurement of particles of the sputtered gold (Au) and analysis of grain size in the deposited film was concluded from the SEM micro graphs (Figure 3). Measured value indicates the surface roughness when gold layer was developed under the sputtering mechanism. The images technically justified the increase of homogeneity due to uniform deposition of gold (Au) on the homogeneous polymer film which ultimately offers enhanced sensitivity to the fabricated film. The deposited surface was observed smooth enough, dense and shown fine structure of surface roughness. As the thickness of the film decreases, the electron collisions with surfaces become important. Figure3. (a) represents homogeneous surface of the polymer film which shows uniform gold (Au) deposition on its surface. Image at Figure 3. (b) indicates surface damage due to high electron beam interaction in a region of ultra-thin film imparted on the sample surface. A cross sectional image of the film at Figure3. (c) represents layer by layer view of the device. Figure3. (d) at the inset demonstrates heterogeneous surface structure of the film.

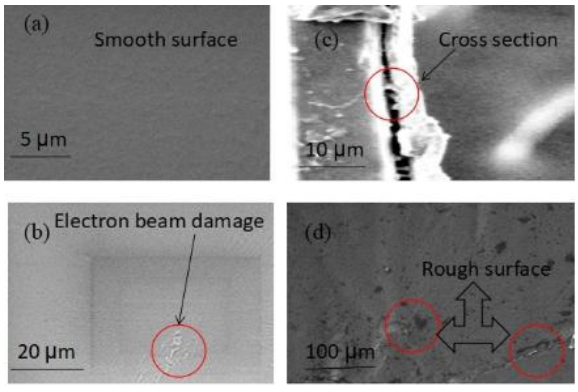

Fig. 3. SEM image of (a) The homogeneous sensor surface of Au template (scale bar, 5 µm) (b) Damaged surface due to high electron beam (scale bar, 20 µm) (c) Cross sectional image of hybrid sensor (scale bar, 10 µm) and (d) Surface Roughness, heterogeneous surface (scale bar, 100 µm).

IJASRM

International Journal of Advanced Scientific Research and Management, Volume 3 Issue 12, Dec 2018

www.ijasrm.com

ISSN 2455-6378

2.4. X-RD Analysis

Experimental observation carried out by X-ray diffraction (XRD, Rigaku 800, table top model) at 2θ vs intensities with varying θ values from 30°-90° and scanning speed of 4 rpm. The X-ray generator was operated at 40 KV and 40 mA respectively. The observed XRD patterns of fabricated films are illustrated in Figure 4. The figureat inset 4.(a) representsGausian normalized curve of polymer based metal electrodes sensor which revealed the crystalline properties of gold (Au) deposited on the polymer. Figure4.(b) indicates amorphaus properties of PDMS alone.

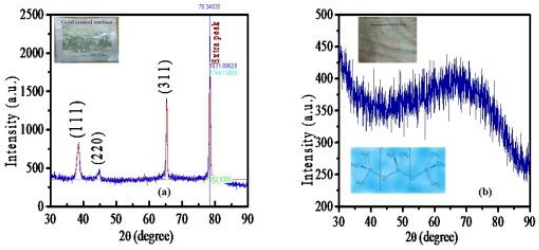

Figure 4. XRD graph of (a) Gausian normalized peak of Al-Au electrode based polymer sensor and (b) PDMS polymer film.

2.5. Measurement of Output Signals Generated from Self potentially enhanced electrode based hybrid thin film sensor

Stress responses of hybrid sensor for different conditions with changing electrode position, stress variability from periodic to random and

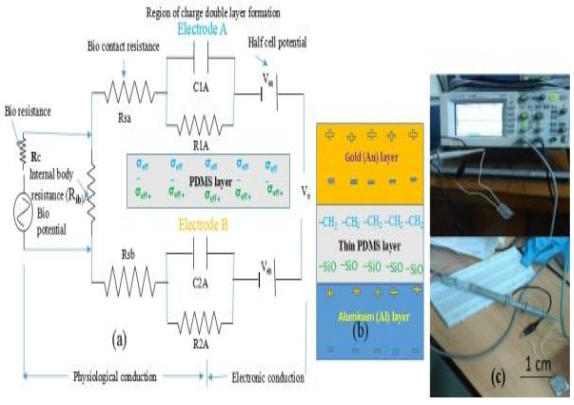

Figure 5 (a) Electrical equivalent of hybrid sensor-Electrode A & Electrode B represent metal electrodes; R1A & R2B are the contact resistances of the materials, Vo is the measurable bio potential, (b) Electronic configuration of contact layers and (c) Physical set up

physiological signals were captured. Copper (Cu) wires were utilized for signaltransmission to and fro the device with measuring system, and it was fixed on both surface of the electrodes by carbon tape. The open circuit voltage and short circuit current from the hybrid sensor under different bio-signals and soft stress were recorded by digital oscilloscope (DSO3102A, Agilent) assembled with Lab view PC based voltage measurement system. Input impedance of the hybrid sensor was measured by conventional AVO meter and verified with bread board based parallel resonance L-C-R circuit attached with trainer kit and frequency generator. All the output were taken using a bridge circuit and a high load resistance to avoid loading effect due to the high internal device resistance. The equivalent circuit diagram along with layer wise internal electrostatic charge polarization phenomenon was described in Figure. 5(a) & (b) respectively. The actual lab based measuring set up represent in Figure 5. (c).

3. Results and Discussion

Three layers film with thin homogeneous surface morphology of polymer is responsible for electrical charge double layer formation on the contact surface of the skin. Physio-electrical phenomenon appears at the interface between gold (Au) and aluminum (Al) electrodes as well as adjacent layer of the polymer as observed. At skin contact boundary, two layers of ions with opposite polarity form, if a voltage is applied. The ions from electrodes layer are separated by a single layer of skin that adheres to the surface of the electrode and acts like a conventional dielectric capacitor. The amount of electric charge stored in the double-layer capacitor is linearly proportional to the applied voltage and depends primarily on the electrode surface. By physiological potential at the bio contact region the electrode generate two layers of polarized ions. One layer is on the surface lattice structure of the electrode and other layer with opposite polarity originates from associated dissolved ions, distributed in the middle layer of thin polymer, that has moved in the direction of the polarized electrode. These two layers of polarized ions are separated by natural potential difference between gold (Au) and aluminum (Al) metals. The metallic mono layer forms the inner Helmholtz plane (IHP), adheres by physical adsorption on the electrode surface and separates the oppositely polarized ions from each other, forming a molecular dielectric. The amount of charge in the electrode is matched by the magnitude of counter-charges in the outer Helmholtz plane (OHP). This is the area close to the IHP in which the polarized ions

are formed. This separation of two layers of polarized ions through the double-layer phenomena store electrical charges as in a conventional capacitor which forms a static electric field in the molecular IHP layer of the nearest molecules that corresponds to the strength of the applied bio potential.Small thickness of the IHP creates a strong electric field 'E' over the separating polymer molecules following the equation,

$$E = U / d \quad \text{---------- (1)}$$

Where 'U' is the potential difference and'd' is the thickness of polymer layer.

Using the early Helmholtz model to calculate the capacitance the model predicts a constant differential capacitance 'Cd', independent from the charge density, even depending on the dielectric constant 'ε' and the charge layer separation 'δ' in,

$$C_d = \varepsilon / 4\sigma\pi \quad \text{---------- (2)}$$

Conventional capacitance can also be measured by using,

$$C = \varepsilon A / d \quad \text{-------- (3)}$$

Where 'ε' is permittivity, 'A'representssurface area of electrode and 'd' is small distance between electrodes.

From conventional equation of charge and potential we get,

$$V = Q / C \quad \text{---------- (4)}$$

Where 'C' represent capacitance, also from standard equation,

$$Q = \sigma \times A \quad \text{---- (5)}$$

$$\sigma = E\varepsilon_0 \quad \text{---------- (6)}$$

Using equation (3) and (6) we get,

$$V = E\varepsilon_0 d / \varepsilon \quad \text{------ (7)}$$

The positive charge on the top surface of the sensor arising from the gold deposition utilized for charge polarization of two material layers. Aluminum foil substrate is electrically negative comparing with gold but positive comparing with polymer which leads to negative charge formation in bottom layer of the film and intends electrical charge polarization in middle layer. Negative charge on the bottom surface of the film attracted by the relatively positive aluminum electrode which results a charge affinity to the formation of bounded electric pole on the polymer surface with $–CH_2$ ions. Pole formation by polymer significantly responsible for high sensitive stress response origination of the $-CH_2$ and −SiO dielectric poles causing to the charge double layer formation in presence of tiny instantaneous bio electric signal. By selecting gold (Au) and aluminum (Al) as conducting media of the hybrid sensor a total depolarization system can be realized at the time of measurement. SEM study indicated the surface property of the sensor. Electron beam damage on the surfaceof the sensor at the time of SEM clarified that the surface thickness was soft and thin enough as a bio compatible. In advance, gold (Au) as electrode element has the advantage intoxication and antibacterial because of its bio compatibility and nontoxic nature. The experimental output reflected that, gold (Au) deposited sensor exhibits ultra sensitive acoustic response and pole reversibility due to high electrode potential difference which enabled the sensor to be used without any side specific to the application contact region, at the same time it was declined the possibility of contact capacitanceformation in other side of the sensor surface which is not contacted with physiological object.

Thus, gold (Au) elements can work as an active agent for the realization of very small change in electronic state of polymer which further provoke the electricity generation from very slight stress. From the high magnification images slight non homogeneity and asymmetry was observed due to two methods of film formation. Comparative analysis of XRD graphs revealed us to conclude crystalline gold and amorphous polymer in the thin films. All diffraction peaks correspond to the planes of gold structure [fcc Au (111), (220) and (311) (JCPDS card No.: 04-0748)]. In Figure 4. (a) the composite XRD graph shown an extra peak at 78° on gold surface is situated just after the completion of normal peaks of the gold particles. This peak relies that, secondary bonding causes negative surface charges on the bottom (σeff−) and the −CH2 dipoles (δeff +) on the top with variation of the amorphous plane to the secondary plane of gold (Au) particles. Practically, the sensor exhibits less sensitivity if stressing on the top surface keeping aluminum (Al) on bottom i.e skin-aluminum (Al) contact offers better physiological responses. The probable cause of this mysterious and unexpected phenomenon in this experiment is that, aluminum (Al) offers higher

IJASRM

International Journal of Advanced Scientific Research and Management, Volume 3 Issue 12, Dec 2018

www.ijasrm.com

ISSN 2455-6378

electron mobility than gold (Au) at the time of external stressing which intends better sensitivity at output region. The static impedance of the sensor revealed us the value within 20MΩ which offers better dynamic linearity of the device. High sensitivity of the sensor was observed by human sensation such as normal heart beats (keeping it on the Einthoven Triangle of chest), normal blood pressure (by keeping it under the hand cuff), human breathing, intercostal muscle movement, slight touchand slow sounds.The Figurein 6. (a1), (b1), (c1) & (d1) demonstrate output response of the sensor from very tiny bio-signals within Millie volt range.

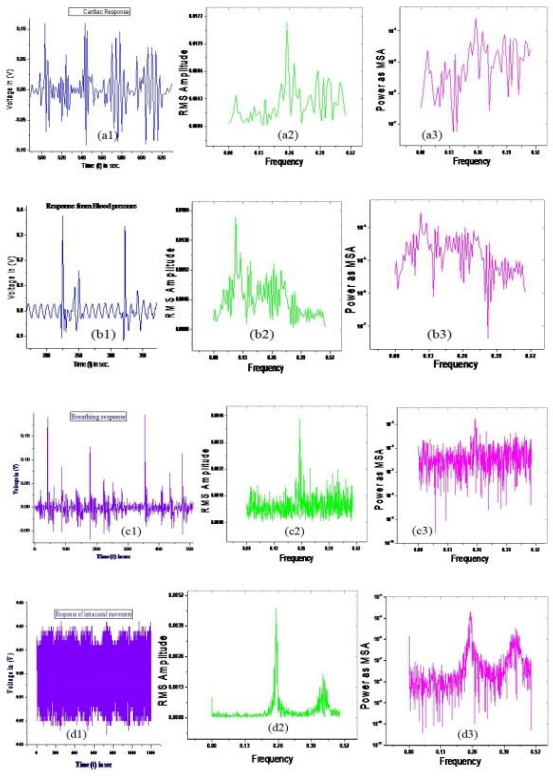

Fig.6. Output response in Volt (a1, b1, c1 & d1) of fabricated PDMS based Al-Au sensor and its FFT in RMS amplitude (a2, b2, c2 & d2) and Power MSA (a3, b3, c3 & d3) with respect to frequency from input of cardiac beats, Normal blood pressure,Human breathing and intercostal

The corresponding fast Fourier transform (FFT) of the output signals in terms of root mean square (RMS) amplitude in Figure6. (a2), (b2), (c2) & (d2) and mean squared amplitude (MSA) power in Figurein 6. (a3), (b3), (c3) & (d3) with respect to frequency indicate change in output responses with slight change in input. The generated output from human finger touch at 10 KPa stress (σa) revealed 3.5 V open circuit voltage (Voc) and short circuit current (Isc) of 0.075 μA. Furthermore, when σa was increased to 20 KPa, the output increased to 5 V and 0.124 μA respectively. In this work, the amount of gold (Au) were very less and it seems that the developed method is economic for achieving high response from very low bio signals with wide range of applications. Output performance of the device demonstrates an alternative design technique for delicate applications.

4. Conclusions

Self potentially enhanced electrode based hybrid thin film sensor was fabricated by utilizing the property of high natural potential difference between aluminum (Al) and gold (Au), separated by thin layer of PDMS film along with charge double layer formation on the bio contact region of the device. Alike output responses were investigated in the opposite polarity direction with several mechanical stress inputs such as music melody, air pressure and streamline tap water pressure. Simple and effectivefabrication technique is pioneering a new horizon of bio medical device fabrication. High performance of the hybrid sensor provides a breakthrough to fabricate Apnea Detector for respiratory function test, tissue phantom preparation for tracking the particles by Optical Coherence Tomography (OCT) in Optical coherence electrograph (OCE) technology for determining tissue bio-mechanical properties and sensitive artificial skin.

Acknowledgments

This work was technically andfinancially supported by Dept.of Instrumentation Science and ONPDL Lab, Department of Physics, Jadavpur University. There is no conflict of interest for any financial benefit.

References

[1]. Carr J Joseph, Brown M John, Introduction to Biomed. Equip. Technol. (Pearson Publication 2001) 102.
[2]. Khandpur SR, Hand Book of Biomed. Instrument. (Tata McGraw Hill Publication, 2nd Edition 2011) 109.
[3]. Kuo A C M, Polymer Data Handbook (Oxford University Press 1999) 411.
[4]. Chopra KN, Maini AK, Thin films and their application in Military and civil sectors (DRDO monographs 2010) 49.
[5]. Geon Hwang-Tae et al, Adv. Mater.26: 4880, 2014.
[6]. Kap Kim Jin,You Chang Min, Yoon Sun, Hyun Kim Jeong, Int. Ferroelectrics 107: 53, 2009.

[7]. Chengliang Sun, Shi Jian, Bayerl J Dylan, Wang Xudong, Env. Sci. 44:508, 2011.
[8]. Shyamkumar Prashanth, Rai Pratyush, Oh Sechang, Ramasamy Mouli, Harbaugh E Robert and VaradanVijay, Electronics 3: 504, 2014.
[9]. Chena Weiqiang, Lamab H. W.Raymond, Fu Jianping, Lab Chip 12: 391, 2012.
[10]. Kim Cheol-Hee, MengYao, Chung-Soo Gi, Intech Open 3: 41, 2011.
[11]. Wua-YaWen, Bianb Zhi-Ping, Wanga Wei, Jun-Jie Zhu, Sensors and Actuators 147: 298, 2010.
[12]. Akbari Ali Mohammad et al, BioMed. Engineering 10: 109, 2011.
[13]. Thangawng LAbel, Ruoff S Rodney, Swartz Amelody, Glucksberg R Matthew, Biomed. Microdevices 9: 587, 2007.
[14]. Zhang Lingqian, Sun Han, Wu Yuanjian, Li Wang Dachao Wei, Zhang Alice Haixia, Wu Wengang, Li Zhihong, Proc. of 17th Int. Conf. on Miniaturized Systems for Chem. and Life Sciences 27, 2013.
[15]. Preetha Jothimuthu, Carroll Andrew, Ali Asgar, Bhagat S , Gui Lin, Markand E James, Papautsky Ian, J. Micromech. Microeng.194: 5024, 2009.
[16]. Yu K. Han Y, R S of Chemistr, 2: 705, 2006.
[17]. Fernandes M. S. et al, Proc. of 32ndAnnu. Int. Conf. of the IEEE EMBS Buenos Aires, Argentina 4, 2010.
[18]. Sasaki A, Furuya A, Shinagaw M, Sens. Actuator 151: 1, 2009.
[19]. Toepke, Beebe M.W, Lab Chip 6: 1484, 2006.
[20]. Kim, Chaudhury J, Owen K M, J. Colloid Interface Sci 244: 200, 2001.
[21]. Abel L. Thangawng, Rodney S. Ruoff, Biomed. Microdevices 9: 587, 2007.
[22]. D. Y. Lee, D. H. Lee, H. S. Lim, J. T. Han, K. Cho, Langmuir 26: 3252, 2009.
[23]. Makamba H, Hsieh YY, Sung WC, Chen S H, Anal. Chem 77: 3971, 2005.
[24]. Yu K, Han Y, Soft Matter 2: 705, 2006.
[25]. C Xu, R Inai, M Kotaki, S Ramakrishna, Tissue Eng. 10: 1160, 2004.
[26]. K Yoon, K Kim, X Wang, D Fang, B S Hsiao, B Chu, Polymer 47: 2434, 2006.