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FABRICATION AND CHARACTERIZATION OF PIEZOELECTRIC P(VDF-TrFE) THICK FILM ON FLEXIBLE SUBSTRATE

Khoon Keat Chow[1,2], Swee Leong Kok[2] and Kok-Tee Lau[3]
[1]Department of Electrical Engineering, Politeknik Ungku Omar, Ipoh, Perak, Malaysia
[2]Faculty of Electronics and Computer Engineering, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia
[3] Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Melaka, Malaysia
E-Mail : markchowmy@yahoo.co.uk

ABSTRACT

In this paper, the fabrication step of poly(vinylidene fluoride) trifluoroethylene P(VDF-TrFE) thick films deposited on flexible substrate are being described using rod Mayer method. Polyester film being used as the substrate where a sandwiched layer of electrode-piezopolymer-electrode thick film is deposited on. The thick-film is then annealed at 100 °C and polarized at 100 V for the film with a thickness of about 18µm, being inspected under EDX, FESEM and XRD. The flexible piezoelectric transducer is able to generate a maximum output power of 0.711µW at an external electrical load of 1MΩ with a maximum peak voltage of 843mV when pinching between two fingers with a force of 5N.

Keywords: polymer, piezoelectric sensor, energy harvester.

INTRODUCTION

Piezoelectric material generates electrical energy charges proportional to mechanical stress that is applied on it, which it is known as direct piezoelectric effect, while indirect piezoelectric effect happen when electrical voltage is applied on the piezoelectric materials and resulting in mechanical deformation. Piezoelectric materials have been widely used for sensor applications such as biomedical engineering, smart sensor detection, and flexible electronic applications [1]. The polymer piezoelectric materials have many advantages over ceramic PZT and become popular after the discovery of piezoelectricity in polyvinylidene reported by Kawai in flexible applications in 1969[2]. One of the advantages of polymer piezoelectric materials is that easily can be fabricated at lower annealing temperatures compared to ceramic piezoelectric such as KNN and $BaTiO_3$. This property make them attractive for piezoelectric applications on flexible substrate, although there are few known fact that piezoelectric polymers have much lower piezoelectric coefficients compared to ceramic piezoelectric. PVDF and PVDF-trifluoroethylene (PVDF-TrFE) are piezoelectric polymers with lower piezoelectricity compared to ceramic based piezoelectric material such as PZT but can conform to complex structural surfaces due to their polymeric nature [3].

The disadvantage of the PVDF piezoelectric materials is that it requires mechanical stretching, which is not suitable for conventional micro-fabrication processes [4]. P(VDF-TrFE) in other hand consists of crystalline structure and therefore the piezoelectric properties depend on the molecular proportion x of vinyledene fluoride in P(VDFxTrFE1−x). The presence of TrFE in the copolymer of the PVDF-TrFE film introduces significant features to the PVDF homo-polymer. One of the advantages of PVDF-TrFE is that it increases the tendency to crystallize in the polar β-phase without the requirement of mechanical stretching to transform the non polar α-phase to the polar β-phase as in the case of PVDF, when $0.6 < x < 0.85$ [5].Among the PVDF-TrFE copolymers, the copolymer at composition near 75/25 mol.% exhibits the highest ferroelectric responses [6-7];

This paper reports the microstructure, phase composition, the result of screen-printing techniques with rod mayer for fabrication of flexible thick film and the voltage signal response to finger pinching of P(VDF-TrFE) film was studied for motion sensor application.

Fabrication steps of sandwiched electrode-piezopolymer electrode

P(VDF-TrFE) thick films in this work was prepared using Poly(vinylidene fluoride-trifluoroethylene) with a molecular weight of 350,000 $gmol^{-1}$ or [70:25mol%] manufactured by Kureha, Japan. Prior to the thick film fabrication, P(VDF-TrFE) (70:25mol %) powder were dissolved in *N,N*-dimethylformamide (DMF), with a concentration of 30ml.

The P(VDF-TrFE) powder was prepared according to the designated weight in percentage of 15wt%. The powder was dissolved in DMF and mechanically stirred at 100 °C for 1 hour. The solution was then immersed in an ultrasonic bath for 20min to ensure that the solution was fully dissolved. Then it was used to deposit a thick film to an approximation of 250µm thick by using mayer rod coating method (RDS #44 wire size, R.D. Specialties) on a flexible polymer (Melinex® 723) substrate with thickness of 75 µm. The thick film was dried under infra-red light for 15 min with a temperature of 60 ˚C in order to remove the residual solvent.

Prior to the P(VDF-TrFE) deposition, first palladium-silver electrode layer were screen-printed using screen stencil onto the blank Melinex® 723 substrate. The second palladium-silver electrode layer was applied after the infra-red light treatment. The thick film was subsequently annealed in an ambient environment oven at 100 ˚C for 1 hour to obtain a smooth and crystalline surface with reduced porosity [8]. The paste materials and their curing methods used in this study are shown in Table-2. Electrical poling was performed across the thick films using D.C. power supply at 100 V for 20 min at 100

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°C (near to the Curie temperature of P(VDF-TrFE). This polarization is to align the domain dipole according to the polarity of the DC voltage. Figure-1 shows the sequence of processes involved in this paper.

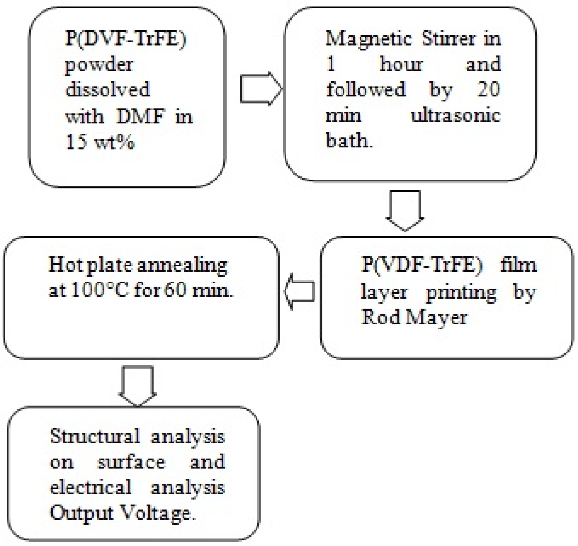

Figure-1. A sequence of experimental procedures.

A schematic diagram of the sandwiched thick film is illustrated in Figure-2 which is being used for the experimental testing in the next step [9-10]. The process parameters are summarised in Table 1 with dimension of the fabricated sensor and electrode layers is shown in Table 2.

Table-1. Summary of paste properties and printed layer process parameters.

Name	Materials	Printing methods	Curing conditions
Top and bottom electrode layer	Palladium Silver Cond-uctor Paste	Print screen	Infa Red 80°C,30min
P(VDF-TrFE) layer	Poly(vinyli-dene fluoride trifluoroethyl ene	Rod Mayer	Infa Red 80°C, 30 min, at plate annealing 100°C
Melinex layer	Polyester film	-	-

Table-2. Dimension of fabricated sensor device.

Design	Parameter, *L* x *W* (mm)
P(VDF-TRFE) layer	2.5 x 2.0
Top Electrode	3.4 x 1.0
Bottom Electrode	3.4 x 0.8

The electrical charges will be generated when the device is subjected to mechanical force, *F*. The electrical charges are measured in term of a voltage, *V* , across the terminals is given as,

$$V = \frac{Q}{C} = \frac{DA}{C} = d_{31} \frac{F}{l}\left(\frac{1}{\varepsilon_{33}^{T}}\right) \qquad (1)$$

where *Q* is the electrical charges, *C* is the capacitance, *D* is the charge density, *A* is the area of the device, *l* is the length of the device d_{31} and ε_{33}^{T} are the charge constant and permittivity of the piezoelectric material respectively.

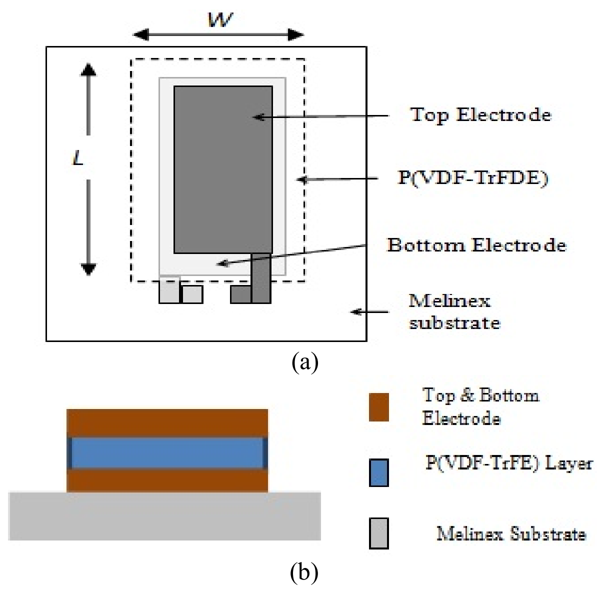

Figure-2. (a) Plan view and (b) side view of the schematic diagram of the sandwiched thick film.

The surface microstructures of the deposited layers were examined by using Field Emission Scanning Electron Microscopy (FE-SEM, accelerating voltage = 3 kV, Model: Merlin, Carl Zeis AG). The phase composition was investigated using glancing angle X-Ray Diffraction (Cu Kα radiation, glancing angle = 1.5°, scanning speed = 6°/min, Model: X'pert PRO, PANalytical B.V.).

Microstructure inspection and characterization

Figure-3 shows the EDX spectrum of P(VDF-TrFE) films with nominal heterogeneities. The elemental composition composed of F, C, Ag, and Pd elements. It is confirmed that P(VDF-TrFE) and palladium silver conductor paste are successfully printed on the Melinex polyester film.

Figure-4 show the cross-sectional morphology of printed P(VDF-TrFE) thick film was measured and checked by using FESEM after completing the printing process and the results are shown in Table 3. It The presence of a gap of 6.5 µm before and after the hot plate annealing due to the weak bonding deposition of palladium silver conductor paste in bottom electrode with Melinex® substrate.

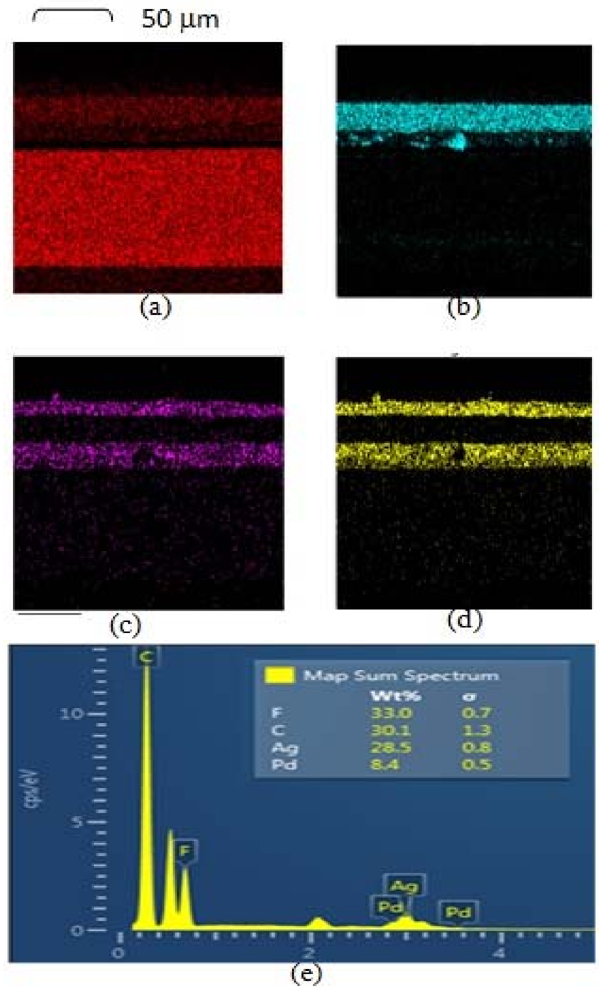

Figure-3. (a) Fluoride, (b) Carbon, (c) Palladium, (d) Silver and (e) EDX spectrums for P(VDF-TrFE) film.

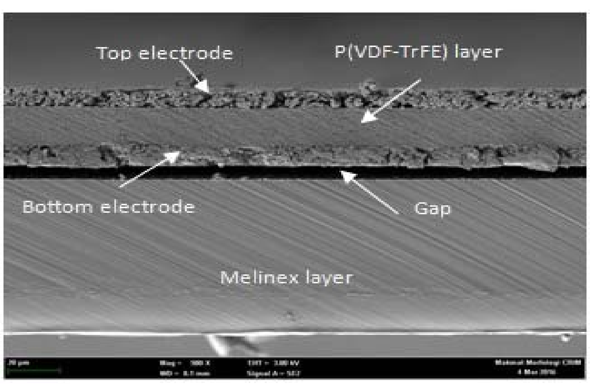

Figure-4. FESEM images of P(VDF-TrFE) film.

Table-3. Measured layer thicknesses.

Layer name	Bottom electrode	P(VDF-TrFE)	Top electrode
Thickness (µm)	10.50	17.64	9.38

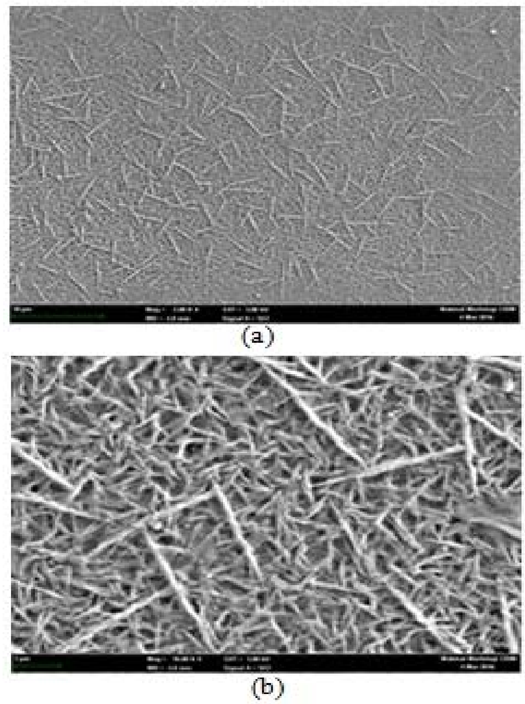

Figure-5. FESEM images of P(VDF-TrFE) film annealed at 100 °C with (a) 2K magnification and (b) 20K magnification.

The quality of printed PVDF layers on Melinex® substrate can be examined by using optical microscopy to determine any evidence of cracks in the PVDF layers [11]. Figure 5a shows the surface microstructure of the annealed P(VDF-TrFE) thick films we observed using FESEM at accelerating voltage 3kV with 2K and 20K magnification. It was found that fine cracks before and after the annealing process (Figure-5b) are probably due to the unsuitable heating treatment in between the Melinex® substrate and P(VDF-TrFE) layer on hot plate annealing method. In thick film technology, common crack occurs where the paste has failed to melt and re-flow during the curing stage [12]. A solution to reduce cracks on P(VDF-TrFE) is a higher temperature or prolonged curing time during the fabrication process.

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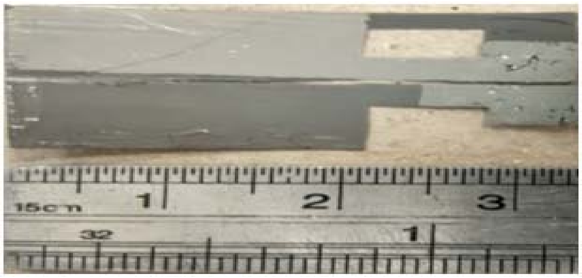

Figure-6. Fabricated sensor piezoelectric P(VDF-TrFE).

The fabricated sensor device of the sandwiched P(VDF-TrFE) thick film illustrated in Figure-6 which is being used for direct measurement of piezoelectric coefficient. Figure-7 show the piezoelectric *d*33 coefficient was measured by using direct measurement (Model ZJ-6B Quasi-Static Piezo d33 /d31 Meter, Institute of Acoustics Chinese Academy of Sciences) and Figure-6 shown the value of piezoelectric coefficient, *d*33, 13 pCN^{-1}.

Figure-7. Direct measurement of piezoelectric coefficient, *d*33.

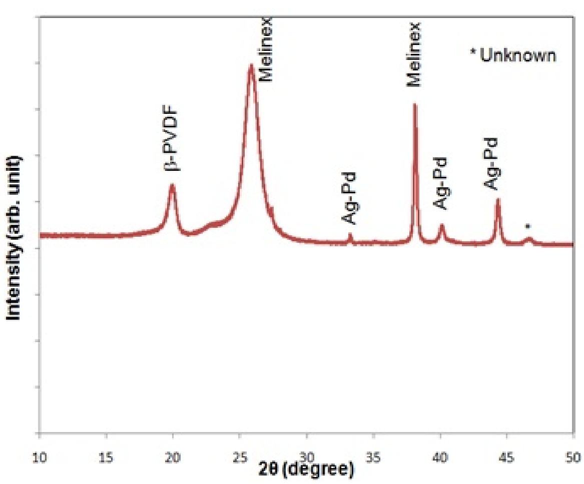

Figure-8. X-ray diffraction patterns from 17.6-µm thick (VDF-TrFE) film.

The Figure-8 show the X-ray diffraction patterns of fabricated P(VDF-TrFE) with presence of β- PVDF, Melinex, and palladium silver. The diffraction peak in the XRD patterns with β-PVDF, appeared at 2θ = 20.03° assigned to (110/200) reflection planes [13-15].

EXPERIMENTAL SETUP

A simple experimental setup was conducted to measure the output of the flexible micro-power generator by pinching between two fingers until both ends of the flexible substrate meet each other. The force's magnitude applied by the fingers was estimated by substituting the fingers forces with incrementally loaded mass weights that placed on the flexible substrate until both substrate ends touched. The output from the flexible micro-power generator is measured using a digital oscilloscope as shown in Figure-9. The result shows that the peak-to-peak voltage output signal varying between ±1V when a force of average 5N is being applied to the polymer sensor due to the bending and stretching movement of a finger.

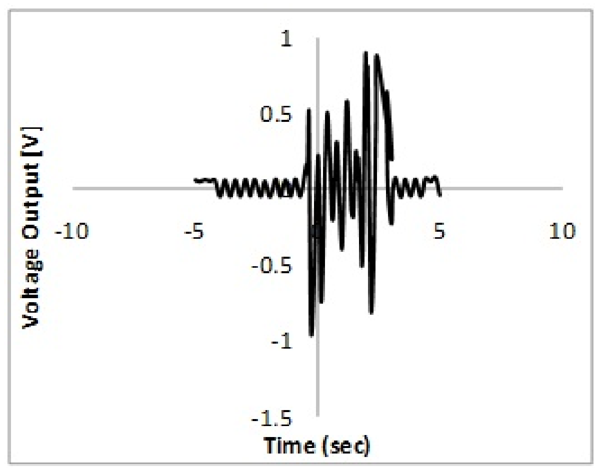

Figure-9. Output voltage from finger movement.

The output power of the flexible sensor is can be evaluated by using an equation,

$$P = V/R^2 \tag{2}$$

where V is the output voltage across a 1MΩ external load resistor R_L. Based on the experimental output voltage, the average output voltage is 843mV and therefore the output power can be calculated as 0.711µW from a single layer P(VDF-TrFE) micro-power generator.

CONCLUSIONS

In this paper, piezoelectric P(VDF-TrFE) thick films were successfully fabricated and polarized simultaneously onto the Melinex polyester substrate as sensor generator using the rod Mayer method. Repeated and consistent experimental results of output voltage up to 843mV has been generated under bending and stretching movement with an estimated force of 5 N, of which the output power can be calculated as 0.711µW.

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