Spray Deposition of PVDF Layers with Application in MEMS Pressure Sensors

Georgi Kolev[1], Mariya Aleksandrova[1] and Krassimir Denishev[1]

Abstract – **Layers of piezoelectrical polymer polyviniliden fluoride (PVDF) were prepared by spray deposition technique on silicon and glass substrates. The temperature of substrates and concentration of the solution were investigated and their influence on the adhesion to the surface and the film's morphology were explored. The pre- and post temperature treatment of the sample was conducted and changes in the layer's behaviour was detected.**

***Keywords* – PVDF, Pressure sensors, MEMS, Piezoelectric effect.**

I. Introduction

With the microelectronic progress it has been observed decreasing of topology's dimensions of the integrated circuits (respectively the entire electronic device) and integration of microsensors and actuators together with the processing electronics modules [4]. Thus, it could be produced completed and individual as functions complex systems. From another side the researches in the microelectronics field are connected with using of new materials, having properties and parameters beyond of already known, which are standard used until this moment.

Nowadays, many scientists work in the area of new material synthesis. The developed new organic polymers expand their application in many sensors and actuators [2]. Recently data about poly(vinyliden fluoride) (PVDF) with piezo- and pyroelectrical properties appear in the literature [3]. The wide application of PVDF as piezoelectric layers in pressure and force sensors and actuators is conditioned from its ability for low cost and simply methods of deposition onto standard substrates. The PVDF possess forward and reverse piezoelectric effect, which make it very suitable material in MEMS structures. It is resistant to many organic solvent and acids, which is big advantages in technologically aspect.

The layers deposited by spray technology are characterized with higher uniformity in comparison with the other popular techniques for solution deposition (for example spin-coating, dip coating and casting) [7]. There are no restrictions about the coverage quality over any size of the covered substrates, because of its operational principle based on fine aerosol stream with controllable spot. The thickness of the produced layers also can be easy controlled and can vary in wide range – from several nanometers to several hundreds of nanometers.

In this paper we aim to investigate the behavior of PVDF material dissolved in MEK solvent in different ratios and to deposit the solution by spray method at different substrate's temperatures. We expect different adhesion of the layers as well as different surface morphology. Our purpose is to find the optimal deposition, pre- and post deposition conditions for obtaining of highly adhesive and uniform films on any type of surfaces used typically in the microsystems (silicon, glass).

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II. Experimental Section

Poly(vinyliden fluoride) (PVDF) is semicrystalline polymer with typical melting point about 160-170 ^oC. Because it contains only a single type of repeat unit, in pure form it is homopolymer. When crystalline and amorphous PVDF phase is combined, layers with properties like high plasticity and chemical resistance to acids and bases are created. The thickness of the layers is variable from x.100 nm to 10μm, mono- and bi-orientated, where the first has isotropic piezoelectric properties, and the second one - anisotropic properties (more information could be found in [6]).

TABLE I
Parameters of the PVDF material

Symbol	Parameter		PVDF	Copolymer	Units
t	Thickness		9, 28, 52, 110	<1 to 1200	μm (micron, 10^{-6})
d_{31}	Piezo Strain Constant		23	11	10^{-12} $\frac{m/m}{V/m}$ or $\frac{C/m^2}{N/m^2}$
d_{33}			-33	-38	
g_{31}	Piezo Stress constant		216	162	10^{-3} $\frac{V/m}{N/m^2}$ or $\frac{m/m}{C/m^2}$
g_{33}			-330	-542	
k_{31}	Electromechanical Coupling Factor		12%	20%	
k_t			14%	25-29%	
C	Capacitance		380 for 28μm	68 for 100μm	pF/cm^2 @ 1KHz
Y	Young's Modulus		2-4	3-5	$10^9 N/m^2$
V_0	Speed of Sound	stretch:	1.5	2.3	$10^3 m/s$
		thickness:	2.2	2.4	
p	Pyroelectric Coefficient		30	40	$10^{-6} C/m^2 {}^oK$
ε	Permittivity		106-113	65-75	$10^{-12} F/m$
$\varepsilon/\varepsilon_0$	Relative Permittivity		12-13	7-8	
ρ_m	Mass Density		1.78	1.82	$10^3 kg/m$
ρ_e	Volume Resistivity		$>10^{13}$	$>10^{14}$	Ohm meters
$R_{\square}$	Surface Metallization Resistivity		<3.0	<3.0	Ohms/square for NiAl
$R_{\square}$			0.1	0.1	Ohms/square for Ag Ink
tan δ_e	Loss Tangent		0.02	0.015	@ 1KHz
	Yield Strength		45-55	20-30	$10^6 N/m^2$ (stretch axis)

For deposition of PVDF layers by spray method, laboratory stand was designed (Fig.1), which consists of adjustable flat heater with power 350 W, placed on dialectical ceramic substrate. The set temperature is controlled by electronic regulator with pulse width modulation (PWM) principle. The temperature range which can be set is 30-120 ^oC and the accuracy in this range is 2 ^oC.

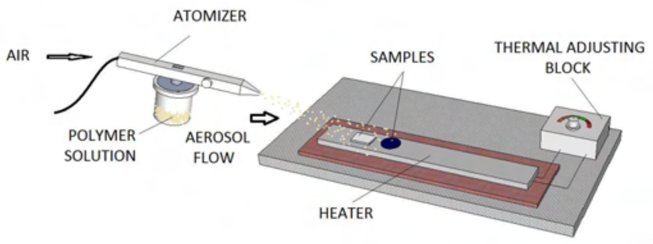

Fig. 1 Experimental setup for spray deposition of PVDF thin films.

According to previously reported experiments this accuracy is high enough to guarantee repeatable parameters of layers, because it is already know that temperature difference more than 10 °C causes difference in morphology. The deposition is conducted by atomizer with possibility to regulate the diameter of the nozzle, which enables formation of aerosol flow with different diameters of the droplets. The working air pressure is 3.8 bars. For obtaining of PVDF layers 5 mm diameter grains were used, purchased from Goodfellow. The used solvent for crystallization of PVDF in β-phase is metil-etil-cetone (MEK).

As the deposition principle is connected with generation of aerosol flow, the uniformity is determined by the density of this flow and the angle under which it falls on the substrate's surface. The kinetic energy of the pieces is defined by the pressure of the transporting (carrying) air. This pressure can be in certain range, whose optimal value depends on the distance nozzle-substrate. The final layer quality is related with the substrate temperature and concentration of the solution. The dependence between initial aerosol diameter and final diameter of the pieces, forming the layer on substrate is given by Eq. 1:

$$\left(\frac{d^*}{d}\right) = 0{,}32T^{0{,}11}P^{0{,}003}C^{0{,}31} \quad (1)$$

By experimental investigation of the optimal pressure, it has to be taken into account that the temperature of evaporation of the solvent (for MEK 70 °C). If the pressure is lower than the optimal, the pieces don't possess the necessary kinetic energy to reach the substrate. Their energy is taken away from the pieces of the surrounding environment. When the energy is higher than the optimal, respectively the pressure is also higher and the aerosols penetrate inside the already deposited monolayers, worsening the layer uniformity and planarity.

III. Results and Discussion

Before deposition the substrates were preliminary cleaned in standard detergent solution consists of hydrogen peroxide, ammonia and distilled water. That prepared substrates were sprayed at room temperature of 20°C with cycles of 3 times and 6 times. The deposited layers were observed under microscope(Fig.2). They are characterized with uniformity and density of the structure. The layers show strong adhesion to the substrates.

Fig. 2 PVDF layers sprayed at 20°C on glass substrate.

Fig. 3 PVDF layers after thermal treatment at 180°C.

After thermal treatment of the samples at 180°C for 30s are not seen vastly change in the morphology, but adhesive properties are worsen. Because of the production of thin films the numbers of mono layers were increased at 10 spraying cycles. In this way denser and more uniform layers were produced(Fig.3). To decrease the monolayers splitting, heating of the substrates to 180°C was necessary (around the material melting point).

During pulverization, the substrates are gradually cooled with the time, because of the solvent evaporation. In this way, however, the adhesion of the monolayers to each other is decreased. The possible reason for this behavior is the straying of the temperature away from the melting point of PVDF(Fig.4). After the adhesion test, the upper monolayers, which are deposited at the lower temperatures, drop off.

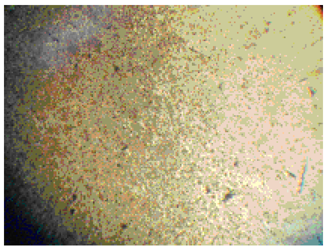

Fig. 4 Adhesion test of PVDF layers

For this reason it is necessary to maintain and compensate the substrate temperature all the time during the deposition process for every spraying cycle. For comparison on the figures below are shown layers deposited at different temperatures in the range 70-100 °C for experimental determination of the most suitable heating temperatures for the substrates. At increased solution concentration (Fig.5), layers pulverized at 80 °C are smooth and uniform, but the adhesion is considerably worsened.

Fig. 5 PVDF layers sprayed at 70 °C on glass substrate (in left) and silicon substrate (in right), having lower adhesive strength.

Fig. 6 PVDF layers sprayed at 80 °C on glass substrate (in left) and silicon substrate (in right), having higher adhesive strength.

Fig. 7 PVDF layers sprayed at 100 °C on glass substrate, showing good adhesion, but low planarity and uniformity.

Fig. 8 PVDF layers sprayed at 80 °C and increased concentration on glass substrate, showing good adhesion, but low planarity and uniformity.

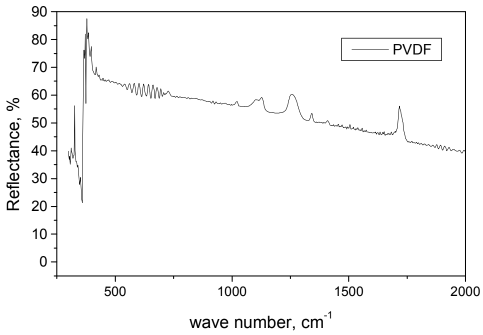

Fig.9 FTIR spectrum of PVDF deposited at optimal spraying conditions.

For chemical identification of the obtained material's phase after deposition and for ensuring that the polymer is not with damaged chemical bonds, a Fourier Transform Infrared analysis (FTIR) was performed (Fig.9). The samples are treated in reflectance mode, because the polymer is not transparent for the infrared wavelength. According to the measured spectrum and the peak positions it can be conferment that the temperature treatment doesn't influence on the changing of the polymer's physico-chemical properties [1], but only on the layer's morphology.

IV. CONCLUSION

From the conducted experiments, it was established the optimal spraying temperature, at which PVDF layers for potential sensing applications are successfully fabricated. The observed adhesive behavior to different surfaces (the most used in microsystem technologies – glass and silicon) depends on the substrate temperature and the solution concentration. It was found that 80 °C is the most suitable temperature. When the temperature gradient occurs, the adhesive strength is worsened. The future work will be connected with investigation of the piezosensitivity of pressure sensing structures, consisting of pulverized layers. It will be determined the connection between the deposition conditions and the sensor properties of the structures.

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