Influence of the Polarization on Some Dielectric Parameters of Thin PVDF Layers

Yordanka Dilyanova Vucheva, Georgi Dobrev Kolev, Mariya Petrova Aleksandrova and Krassimir Hristov Denishev

Abstract - **Thin polyvinylidene fluoride (PVDF) layers were received by spray deposition technique on polyethylene terephthalate substrate and then were polarized with voltages in range of -40V to +40V. The influence of the polarization on the dielectric parameters of PVDF layer was defined by the capacitance - voltage characteristics, which were measured at 1kHz and 100kHz.**

Keywords – **PVDF, Polarization, Capacitance-voltage measurements, Piezoelectric materials, MEMS**

I. INTRODUCTION

Piezoelectric and ferroelectric materials play an important role for Micro-electro-mechanical systems (MEMS) and Nano-electro-mechanical systems (NEMS). They are widely used in many areas of technology and science. Piezoelectrics are a class of materials that can transfer mechanical energy to electrical energy and vice versa. The sensors, based on the piezoelectric effect, transform mechanical signals into electrical signals and are used as accelerometers, and for measurements of pressure and vibration. The piezoelectric actuators transform electrical signals into mechanical signals and are used in displacement actuators and force generators [1]. In other words, an input of mechanical energy will produce an electrical polarization. The reverse phenomenon also occurs; applying an electrical polarization will cause changes in dimensions [2].

One of these piezoelectric materials is polyvinylidene fluoride (PVDF). This material is very interesting because of its properties. PVDF has been widely used in engineering applications, due to its favorable chemical and mechanical properties. Properties, such as high piezoelectric coefficient, good flexibility, biocompatibility, low acoustic and mechanical impedance, and light weight, are especially unique for MEMS applications. The polymer PVDF is one of the most widely used piezoelectric materials in the fluoropolymer family [1]. Kawai was the first one to discover, in 1969, a highly noticeable piezoelectric effect on polyvinylidene fluoride (PVDF). This material is the most studied and utilized piezoelectric polymer. However, commercialized piezo films only appeared on the world market in 1981 [3].

PVDF is a long chain, semicrystalline polymer, having the repeat unit (CH_2-CF_2) and it's one of the polymers with at least three crystalline phases, famous for its pyroelectric, piezoelectric and ferroelectric properties. PVDF can form a different crystal, depending on the condition of the crystallization. These different crystal structures include nonpolar α-phase (TGTG), polar β-phase (TTTT) and γ-phase (TTTGTTTG), depending on the chain conformations, as trans (T) or gauche (G) linkages. When PVDF is cooled from the melt, the crystalline phase formed is the nonpolar α-phase with TGTG conformation. The β-phase crystal has all trans conformation that results in the most polar phase among other crystals, being used extensively in piezoelectric, pyroelectric and ferroelectric applications. The β-phase is typically obtained by mechanical deformation of melt-crystallized films. The γ-phase has similar structure to β crystal, however slightly different TTTGTTTG conformation [4].

Dielectric materials will not conduct electricity, but will store or carry charges for short ranges, under the influence of an externally applied electric field. All solids consist of positive and negative charges, so when an electric field is applied, these charges will separate. This separation of charge is called polarization and can be utilized to store or carry charges over short distances. Piezoelectric materials are a particular type of dielectric material capable of using this separation of charge to convert energy. Important elements of piezoelectric materials are dipoles and domains. A domain is a microscopic region of a crystal, in which the polarization is homogenous. In these domains the dipoles of the material are naturally un-aligned, but can be aligned in a common direction by applying a DC electric field for an extended period of time (Fig. 1). This procedure is called "poling" [5].

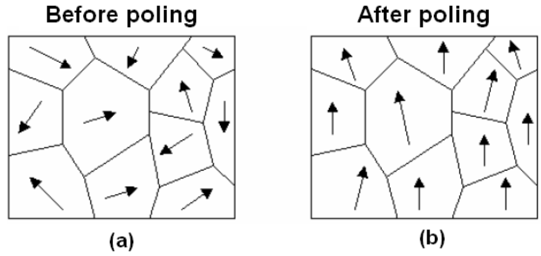

Fig. 1. A diagram of domain structure before (a) and after (b) poling.

Before poling the domains have random orientation. After poling, there is a remnant polarization along the same direction, as the field was applied. PVDF is a non-linear dielectric. This means that when electric field (E) is applied to the material, the stored charge (Q) does not result in a linear response. At lower applied fields, the polarization is similar to a linear dielectric and is fully reversible. As the applied field increases to a saturation point (P_{sat}),

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polarization will remain after the electric field is removed. Polarization saturation (P_{sat}) is the point at which polarization will no longer increase with increasing electric field. The remaining polarization in the dielectric material, after the field has been removed, is called the remnant polarization (P_{rem}). Remnant polarization is basically a measure of the residual alignment in the domains, due to the applied field [5].

For obtaining thin layers of polyvinylidene fluoride for MEMS technology, granules of the material, dissolved in suitable solvent were used. Some organic solvents are methyl ethyl ketone (MEK), dimethyl formamide (DMF) and Dimethyl sulfoxide (DMSO). The techniques, by which could be deposited thin layers for MEMS applications are by casting, spin coating and spray deposition. According to investigations in [6] and [7], can be concluded that, more uniform thin layers of PVDF are these, deposited by spray deposition technique. Therefore the work, presented in this paper is based on investigation of thin PVDF layer, deposited by same technique.

II. Experimental Work

A. Deposition and obtaining of the sample

The experimental work begins with the choice of the substrate. For preparing of the sample, a substrate of polyethylene terephtalate (PET) is chosen, which is stable at temperatures to 110°C. This feature is necessary for the next deposition steps. On the substrate is deposited aluminum (Al) for bottom electrode by thermal evaporation in vacuum chamber A400-VL Leybold Heraeus at vacuum level 10^{-5} Torr. The same material and technique are used for obtaining of the top electrode, too (Fig. 2). The thickness of the electrodes is 200nm, measured by Alfastep Tencor 100. The next step, after receiving the bottom electrode, is deposition of thin polyvinylidene fluoride layer (PVDF). The layer is obtained by spray deposition technique.

PVDF granules, having weight of 1.5 grams (5 mm diameter grains purchased from Goodfellow) were dissolved in 25ml MEK in borosilicate glass vessel. The mixture was heated to 70°C (boiling point of MEK) for 2 minutes. The vessel was closed to avoid evaporation losses from the solution, and after dissolving of the grains, the solution was cooled down on its own to room temperature (25°C). To remove the insoluble polymer particles, the solution was filtered. Very important moment is the insoluble rests of the polymer to be removed immediately after cooling, because fast crystallization at the boundaries solid particles/solution is developed again. If the heating temperature is under the value of 70°C there is no solving process in the vessel [6].

The receiving of the thin PVDF layer was done by experimental setup with atomizer, working with pressure and heater, which heats the samples during the process [7]. The deposition of the PVDF and MEK solvent 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 [7] and the temperature of the heater is 80°C. The thickness of the received thin PVDF layer is 1μm. The top aluminum electrodes have sizes 3x6mm and they are all equal.

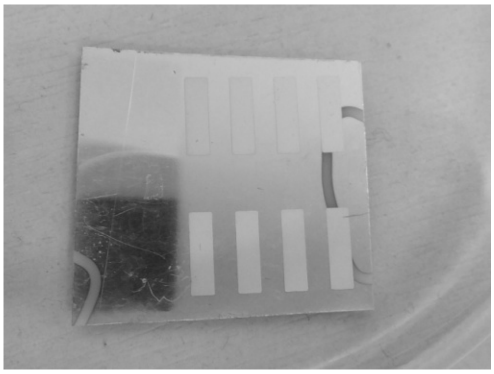

Fig. 2. 1μm PVDF layer on PET substrate with Al top and bottom electrodes

B. Poling and measuring

The polyvinylidene fluoride thin layer, deposited on polyethylene terephthalate substrate was polarized with voltages in the range of -40 to +40V. The influence of the polarization on the dielectric parameters of PVDF layers was estimated by the capacitance - voltage characteristics.

The measuring stand is shown in Fig. 3, and Fig. 4 is a picture of the stand. It consists of XYZ-table with microscope and metal probes, which are connected by a LCR meter and DC power supply.

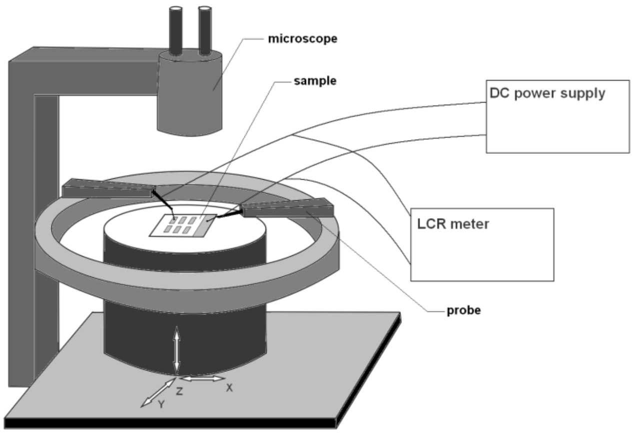

Fig. 3. The experimental set for measuring the capacitance-voltage characteristics

The polarization of the PVDF layer starts with the increasing of the voltage from 0V to +40V. At every value of the range of the increasing voltage the polarization runs for 1 minute and then, the capacitance between one of the top and the common electrodes of the sample was measured. After that, the same was done for voltages in the range between +40V to 0V. The procedure was repeated for voltages 0V to -40V and for voltages -40V to 0V. The capacitance-voltage measurements were done at 1 kHz and 100 kHz and 50mV of the LCR meter.

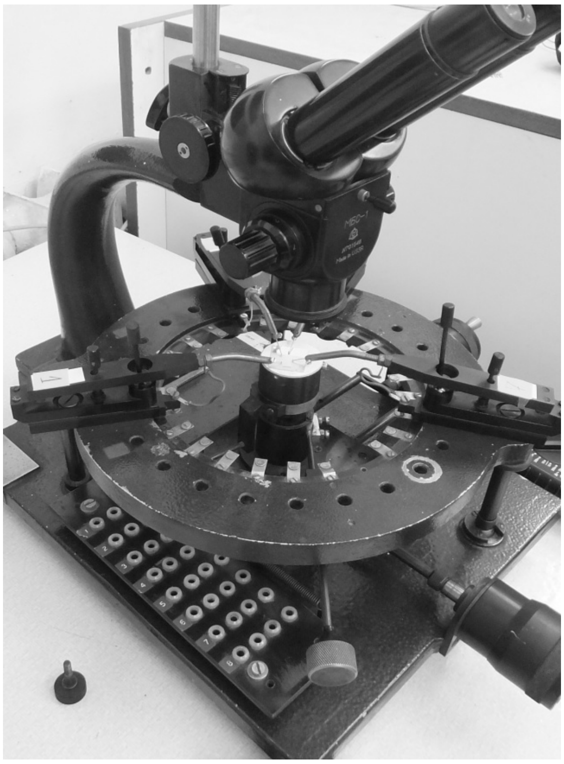

Fig. 3. Stand for measuring

III. Results and Discussion

The capacitance - voltage characteristics were measured for voltages up 0V to +40V, down +40V to 0V, up 0V to -40V and down -40V to 0V. These characteristics are for the bottom and one of the top electrodes. They are shown on the next figures (Fig. 4 to 6). In Fig. 4, the graphics of the capacitance, measured at 1kHz are presented. It can be seen that, in direction up from 0V to +40V, the capacitance has peak at a value of the voltage 4V. At this point the value of the capacitance is 28 pF, but after this point the next values of the capacitance are lower and are close to, the lowest value of 25,109 pF. After that, when the voltage is applied down from +40V to 0V, there are no radical changes in the values of the capacitance but they are lower than these in the forward direction. Here, the maximum and the minimum values are 25,729 pF and 25,126 pF, respectively. In the reverse direction, first in range of voltage 0V to -40V the capacitance has again peaks but downward. Here, the maximum and minimum values are 25,780 pF and 24,101 pF, respectively. The maximum is again at 4V, but at inverted polarity. In direction from -40V to 0V the values of C are close to those in the previous measurements and here maximum and minimum are 25,827 pF and 25,403 pF.

As a conclusion it can be noticed that the maximum values of the capacitance are in the range between 3V to 5V, at any one of the directions. In this range there are also the capacitance peaks.

Analogical measurements were done at 100 kHz, too. The graphics are shown in Fig. 5. It can be seen, that in this case there are again capacitance peaks, similar with these in the previous case. Up to +40V the peak is where the maximum value at this direction is. It is at 4V-22,229 pF. The minimum value is 22,020 pF.

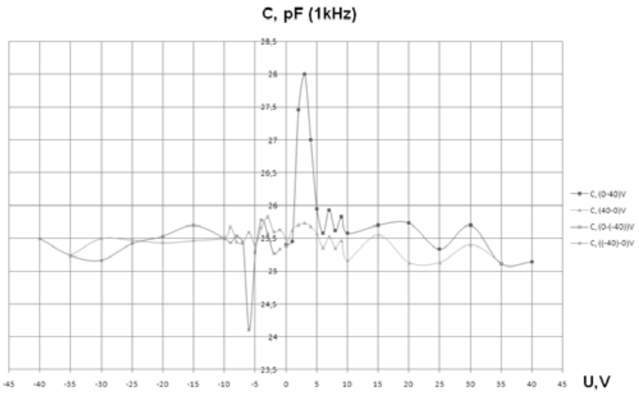

Fig. 4. Capacitance-voltage characteristics at 1kHz

The capacitances, measured backward from 40 to 0V, are very close but higher than these in previous measurement. The maximum here is at 5V-22,233 and the lowest 22,091pF. At the other direction of the voltage, from 0 to -40V, the highest value is again at 4V and is 22,213 pF. In the backward direction the highest and the lowest values are 21,455 pF and 18,237 pF, respectively. The maximum is at 3V. In this case the capacitances are lower than those at the previous case.

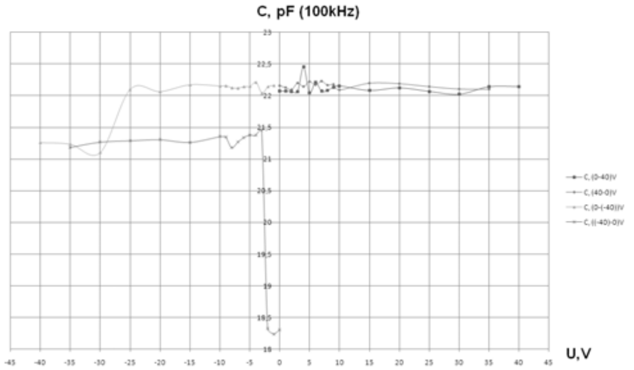

Fig. 5. Capacitance-voltage characteristics at 100kHz

In the Fig. 6 the comparison of the two graphics is presented.

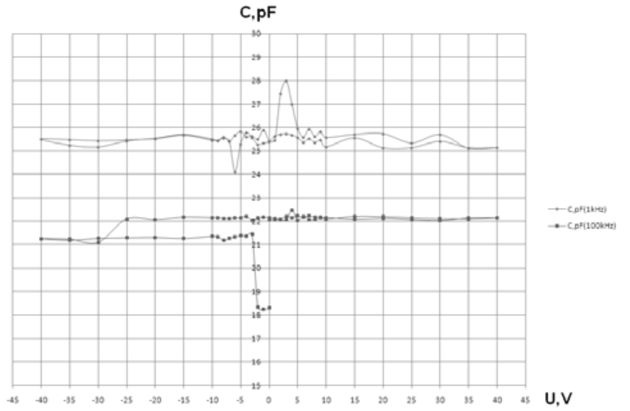

Fig. 6. Capacitance-voltage characteristics at 1kHz and 100kHz

The measured characteristics present that only in range of 3V to 5V the capacitance has peaks and maximum values for the whole measurement. That corresponds with the rotating of the PVDF layer's dipoles.

It can be seen also that, above 5V the capacitance has not any peaks and the polarization to ± 40V is unnecessary.

In conclusion, the polarization of thin polyvinylidene fluoride layer influences on the dielectric parameters of the piezoelectric layer.

IV. CONCLUSIONS

As a result of the investigation, carried out with the PVDF sample it could be concluded that, the polarization of thin polyvinylidene fluoride layer influences on the dielectric parameters of the piezoelectric layer.

Especially for the specific case, for the mentioned PVDF layer thickness, the range of the most effective polarization voltages is between 3V and 5 V. The future work should be done for finding the optimal voltage range.

Better polarization is obtained at lower frequencies – around 1 kHz. The future experiments could be done for finding of the optimal frequency range.

The most effective polarization should be done only once, in forward direction. The next polarization, in the reverse direction, is not good for the structure, and the results, estimated by measuring of the capacitance, are worst.

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