Analysis of the Behavior of PVDF Layers Deposited under Various Conditions

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***Abstract*–We analyze the surface and piezoelectric properties of PVDF films deposited on the surface of Si wafer by solution casting under various conditions of temperature and electric field.**

***Index Terms* – PVDF, Kelvin Probe, AFM**

I. INTRODUCTION

In this paper we present a preliminary study of the piezoelectric properties of polyvinylidene fluoride (PVDF) film materials grown on Si substrate under various conditions. Our targets for this research are to test the possibility to elaborate new ultrasound and piezoelectric sensors, based on PVDF materials.

In 1969, Kawai, [1] have discovered that, applying a strong electrical field on PVDF, the piezoelectric effect can be observed. This was an important step for the development of electro-active polymer sensors. PVDF is a ferroelectric polymer; its dipoles can be „aligned" by an external electrical field, thus polarization is being kept [2].

Such films are intended to be used as pyroelectric and electro-acoustic transducers. Piezoelectric films of this polymer are flexible and have high mechanical strength. Moreover, they have low acoustic impedance that is comparable with one of the biological tissues, a low acoustic resistance and a high elastic constant. Besides, sensors made of PVDF are good for wet environment [3].

This research is relevant to the need for new ultrasonic and pyroelectric sensors for bioengineering applications and other domains where small dimensions sensors are need.

II. METHOD

A)PVDF film

PVDF is a polymer with the degree of crystallization being around 50%. As other poly-crystals, PVDF polymer is a structure with amorphous areas. Addition of copolymer, such as TrFE, highly increases the degree of crystallinity [7]. PVDF film strongly absorbs infrared radiation in the range of 7 - 0.20 microns, corresponding to the wavelength spectrum emitted by the human body. PVDF is mechanically strong and flexible material with a density of approximately 1780 kg/m^3.

To increase piezoelectric response, PVDF film is stretched in one or both directions, so its size increases several times. Elastic coefficients (such as Young's modulus) are determined by the strain. For example, if the film was stretched at 140° C to a 4:1 ratio, Young's modulus is 2.1 GPa, and if the ratio is 6.8:1, the modulus is 4.1 GPa [4]. Another way to achieve high polarization is poling in a strong electric field (over 300 kV/cm), thick films have to be heated in this process up to 100^{o}C.

B)Probe *microscopy*

In scanning probe microscopy, the surface micro-relief and its local properties are explored by scanning with a needle-shaped probe. The tip of the probe has tens nanometers in diameter. The distance between the tip and the scanned area is 0.1-10 nm.

To verify the piezoelectric properties of PVDF material we used a scanning probe microscope Solver P47H-PRO that provides spatial resolution of 0.1nm (as evaluated by minimal scanning step). In comparison with scanning electron microscopy (SEM), atomic force microscope has several advantages. The electronic microscope (SEM) gives a pseudo three-dimensional image for the test area, while AFM give a really three-dimensional topography.

Furthermore, the non-conducting areas viewed by AFM don't need to have a conductive metal layer, which often lead to deformation of the surface. For normal operation in SEM, it is necessary that the sample is placed in a vacuum, while most microscope AFM modes can be implemented in air or even in the liquid. One of the drawbacks is that AFM can scan a small area of the sample [5].

C)Kelvin probe method (MKS)

The Kelvin probe method is used to visualize distribution of the electric potential over the surface of specimen. The Kelvin probe method works in two steps. In the first step the topography is determined. For the second pass, the probe is moved over the sample at certain distance from its surface to determine the surface electrical potential $\Phi(x)$. For this, the console is put into vibrations by applying to the probe a voltage V that contains static and dynamic components.

$$V_{varf} = V_{dc} + V_{ac}\sin(wt) \quad (1)$$

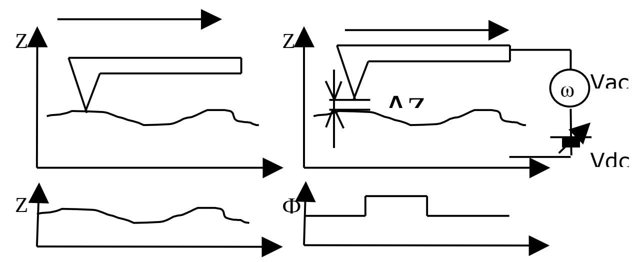

Fig.1.Kelvin probe method (MKS)

The capacitive force, that forces console to vibrate, is given [6] by:

$$F_{cap} = (1/2) * (V_{tip} - \Phi(x))^2 * (dC/dz), \quad (2)$$

where Cz is the capacitance between the sample and console. The force

$$F_{capw} = (dC/dz * (V_{dc} - \Phi(x) * V_{ac}) \sin(wt) \quad (3)$$

which comprises the first harmonic, leads to console oscillations with the same frequency w [5].

For every surface point, the feedback system change DC component of the probe voltage (V_{dc}) until the w component of console oscillation (and w force component) disappears and $V_{dc}(x)$ becomes equal with F(x). Thus the $V_{dc}(x)$ distribution will reflect the surface potential distribution over the sample area.

III. EXPERIMENTS

For our experiments, aimed to obtain cheap and easy-manufactured ultrasonic sensors, the PVDF – TrFE copolymer films (molar ratio 70:30) were deposited on the surface of commercial Si wafer by solution casting. The 1 μl drop of PVDF-TrFE solution in dimethylformamide was placed over the SI substrate and dried in air either at room temperature or at 135°C. Some samples were dried in a weak electric field (600 V/cm).

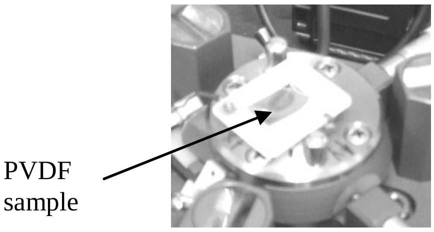

Fig.2. PVDF sample.

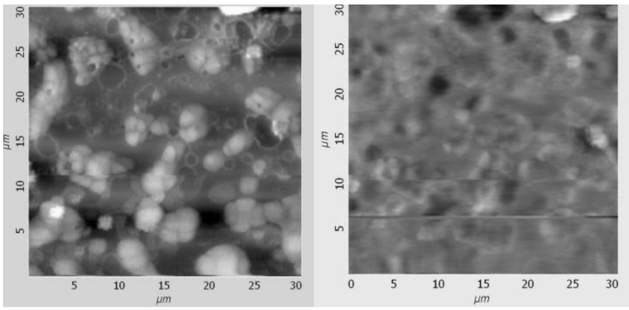

Fig.3. Surface of the sample, crystallised in electric field (E = 600 V/cm,) at the temperature 20^0 C, Scan size 30x30 μm, surface topography (left) range 0÷250nm, surface potential (right) range –60 ÷ +90 mV

The topography of the obtained films as well as distribution of the surface potential can be seen at Fig. 3-5. We used the method of piezoelectric response force microscopy to evaluate piezoelectric response of the film. It is widely applied to study ferroelectric materials and allows exploration of its domain structure. The method is based on the evaluation of the impact of the local electric field under the tip.

The tip is brought in contact with the specimen surface and alternating voltage is applied to the tip. The voltage produces local electric field under the tip, which in turn cause piezoelectric specimen to shrink and expand periodically hereby moving the tip itself.

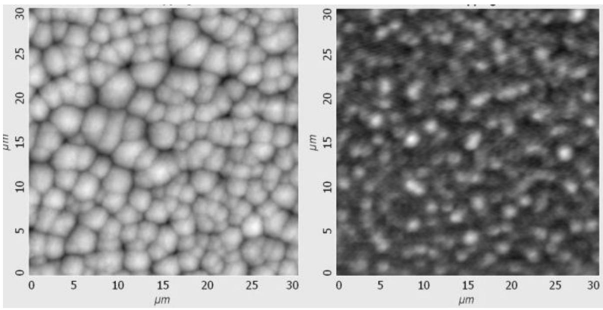

Fig.4. Surface of the sample, crystallised at the temperature 20^0 C, without electric field. Scan size 30x30 μm, surface topography (left) range 0÷150 nm, surface potential (right) range –50 ÷ +180 mV

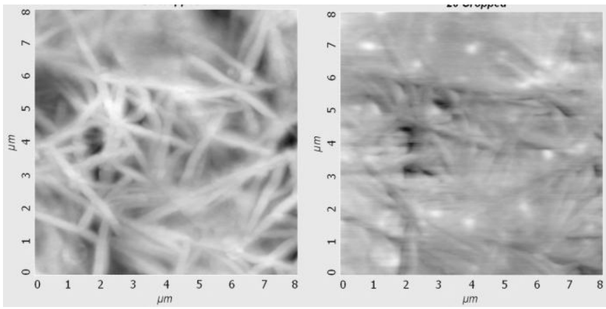

Fig. 5. Surface of the sample, crystallised in electric field (E = 600 V/cm) at a temperature of 135^0 C. Scan size 30x30 μm, surface topography (left) range 0÷300 nm, surface potential (right) range –700 ÷ - 300 mV

Thus the tip will move with the frequency, equal to one of the alternating voltage, while the amplitude of movement depends on the magnitude of electric field, piezoelectric properties of the material and mutual orientation of the electric field and polarization vector of the measured object [6]. The images of piezoelectric response (figs. 6, 7) are obtained by depicting the amplitude of the tip oscillations in arbitrary units.

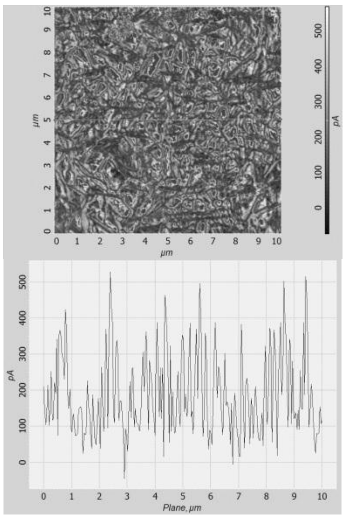

Fig.6. Piezoelectric response (relative units) of the sample, crystallised in electric field (E = 600 V/cm) at a temperature of 135^0 C (left), profile of the sample (right).

Fig. 6 demonstrates piezoelectric response of the obtained PVDF film. Non-uniformity of image implies different piezoelectric properties of small (0.1-0.5 μm) film areas that, probably, may be interpreted as PVDF domains. The different response over the film may be explained by different orientation of the domains. To validate this supposition, additional DC electric potential was applied between the tip and sample. Figure 7 demonstrates increment in magnitude of piezoelectric response due to introduction of both negative and positive voltage. From this, one may suggest, for instance, that PVDF domains are initially poorly oriented. Application of electric field causes them to become more aligned more, thus the specimen under the tip becomes more polarized and its piezo-response increases.

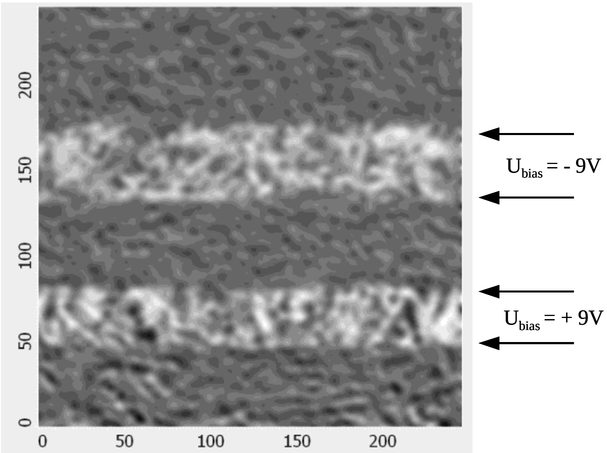

Fig.7. Change of the piezoelectric response of PVDF film (relative units) due to bias voltage applied to the probe (areas indicated with arrows)

IV. CONCLUSIONS

The experimental analysis demonstrated that the piezoelectric properties of PVDF films, grown on Si substrate by solution casting depend strongly on the film growth conditions. Under proper growth conditions, the ferroelectric properties may be suitable for the use in micro-sensors.

V. ACKNOWLEDGMENT

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AUTHORS' CONTRIBUTIONS

The first author (VC) conducted experiments, collected the data under the supervision of the second author and wrote a major part of the paper. The second author (AK) conducted some AFM experiments, provided the whole guidance and planning for the experiments, interpreted results and contributed writing the paper. The third author originated the idea of the study, helped interpreting some of the results and contributed to writing the paper.

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