Influence of the deposition conditions on the morphology of PVDF layers with possible application in MEMS pressure sensors

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Abstract: Piezoelectric films of poly(vinylidene fluoride) (PVDF) were prepared by casting and spin coating on silicon and glass substrates. The effect of the drying temperature and the post-annealing temperature on the film morphology was studied with optical microscopy. It was chosen the optimal combination of deposition conditions, regarding the wetting of the substrate surfaces, uniformity of the produced layers and their adhesion. Planar types of structures, producing surface acoustic waves (SAW) were prepared to establish piezoelectric response after the high temperature treatment of the polymer layers.

Keywords: PVDF, pressure sensors, MEMS, piezoelectricity, SAW

1. Introduction

The combination of microelectronics and mechanical components makes microelectromechanical (MEMS) sensors more powerful and versatile than the conventional sensors. MEMS pressure sensors have been studied by many researchers over the past several years and many articles can be found, concerning sensing mechanisms and materials used for them [1, 2]. Today, many companies fabricate pressure sensors for different applications, for example in automotive electronics, measurement devices, biomedical devices, etc. For pressure sensing, different constructions are designed, where is used flexible element - membrane or diaphragm [3, 4]. They are movable under the influence of the applied pressure, which has to be measured. There are several approaches to register this deflection, for example by using of sensorisitive or piezoelectric effect. Typically, in MEMS pressure sensors, silicon membrane is manufactured by using of two main technologies: by deep silicon etching of the substrate and p++ stop etch layer and by electrochemical etching with p-n-junction. Firstly, film deposition and reactive etching technologies were used to fabricate polysilicon diaphragms with cavities underneath [5]. However, recently, the piezopolymers took an advantage, because of the easy and low cost fabrication [6].

Poly(vinylidene fluoride) (PVDF) is semicrystalline polymer, which is homopolymer, when it is in pure form. Then the material posses phase transition temperature of approximately 160-180°C. During crystallization from solution, PVDF layers with properties like high plasticity and chemical resistance to acids and bases can be produced. Usually, the material exists in alpha-phase. To acquire piezoelectric properties, however, PVDF must pass through state conversion in beta-phase [7]. The process can be accomplished by using of defined organic solvents, like dimethylformamide (DMF) and methyl ethyl ketone (MEK).

Several investigations have been realized in the field of deposition of piezopolymeric layers for sensing elements. Foster and White [8] suggest electrophoretic technology for deposition of PVDF derivative films. They report for repeated cycles of electrophoretic deposition and annealing, necessary to produce dense, 25 μm thick, PVDF derivative films without pinholes or cracks. Kang et al. describe humidity controlled spin casting, combined with rapid thermal treatment, for thin beta-type PVDF film preparation, but for ferroelectric device fabrication [9]. In the paper of Cardoso et al. spin-coating is applied for producing of nanofilms of poly(vinylidene fluoride) with controlled electroactive crystalline phase [10]. As can be seen, several techniques are already developed for obtaining of piezopolymeric thin films, but the adhesion problems, the irregularity of distribution of the grains and distorted output signal (piezo-response) still occur.

In this paper PVDF layers were deposited by casting with overflow and spin coating, and the influence of the thermal treatment over the layer’s morphology and adhesion was investigated. The aim of our investigation was to determine the influence of the substrate type, deposition method and the annealing temperature over the PVDF based solution distribution and layer formation.
2. Materials and Methods

2.1 Preparation of PVDF solution in MEK:

PVDF granules, having weight of 1.5 gr (5 mm diameter grains purchased from Goodfellow) were mixed with 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.

2.2 Preparation of PVDF films by casting:

Before deposition the PVDF:MEK solution was stirred and overnight for obtaining of homogenous mixture. It was observed partially dissolving of the piezopolymer, so additional treatment in ultrasound vane was applied. After second filtration, the solution was cast onto silicon and glass substrates. The substrates were preliminary cleaned in standard detergent solution consists of hydrogen peroxide, ammonia and distilled water. The thin silicon oxide layer formed onto the silicon surface was removed by short dipping in hydrogen-fluoride water solution. The polymer layers were produced by consequently cycles of casting and drying at 90°C for 15 minutes.

2.3 Spin-coating of PVDF:MEK solution:

During spin-coating deposition, the requirement to the solution is to possess certain viscosity. If the solution is too dense the additional quantity of solvent can be added and the mixture must be stirred to be homogeneous. Deposition parameters are centrifugal velocity 500 rpm and duration of spinning 30 sec.

After deposition (for cast as well as for spin-coated films), high temperature annealing at various temperatures was applied for 2-3 minutes for hardening of the polymer bonds and cohesion forces with the substrate. To establish the most suitable post-deposition conditions, several samples were treated until the optimum was found. For conduction of the electrical measurement planar structures with PVDF layer and comb electrodes were prepared.

For the microscopic observations the magnification was 100 times. The power supply for the measurement of the piezoelectrical reaction was low-frequency signal generator ИЗ-109 and the obtained reaction was observed by digital microscope DQ2042CN with frequency range 40 MHz.

3. Results and Discussion

3.1. Influence of the substrate temperature during deposition and the post-annealing treatment on the layer’s morphology

PVDF layer was deposited firstly by casting on non-annealed silicon substrate. After drying at 90 °C in convection oven, the solvent was fully evaporated, because its evaporation temperature is approximately 70 °C. The result is formation of non-uniform layer and after microscopic observation presence of not connected in between particles was established. This leads to irregularities in the deposited film, which are crucial for the contact resistance with the electrodes in the future pressure sensing device (Fig. 1). This enforces the dried layers to be additionally thermally treated at higher temperatures. The layer shown on Fig. 2 was deposited at the same conditions like the first one, but additional post annealing at 180 °C, for several minutes, was applied. At the areas, where the layer is thinner, bad wetting of the substrate surface was observed. The result is forming of bare, uncovered zones, all over the whole substrate area. The polymer particles are collected together, shaping bigger, but still separated aggregates or polymer islands, consists of heaped micro-grains. The layer, formed in this way is not dense, which is precondition for short circuit between the electrodes, when it is incorporated in working structure. To avoid the observed defects we carried out experiments with preliminary heated substrate (Fig. 3) to increase the free surface energy and to improve the overflow of the solution, during the film formation. Therefore, for solvent removing and simultaneous drying and backing, the silicon substrates were preliminary heated, before solution casting, so the heating field influences the film formation in situ during the deposition process. For fixing of the optimal temperature, at which the polymer layer is uniformly distributed, dried and in the same time backed, series of experiments were conducted at different substrate temperatures.
During the experiments with polymer layers deposition, it was established that it is necessary applying of post-treatment temperature near to the temperature of softening of the PVDF polymer grains (180 °C). This temperature is still lower than the typical decomposition temperature of the material, which is approximately 240 °C. The purpose of the thermal field is polymer transition from solid to liquid-viscous state and joining of the separated droplets together in continuous uniform layer. The layer, shown in Fig. 3, is preliminary heated at 200 °C. It was applied neither drying nor post-annealing. It was observed split of the layer, which is indication for too high temperature, leading to fast evaporation of the solvent. This results in arising of internal mechanical stress and microcracks in the layer. At annealing temperatures, very close and higher than the softening point, “burning” of the layer is revealed (Fig. 4).

The main conclusion is that the appropriate temperature of treatment coincide with the produced layer, shown on Fig. 2, but it is necessary repeatedly multiple deposition of the polymer solution, combined with intermediate drying after every deposition until desired density is achieved.

For better observation of the film structure, samples deposited by casting on glass substrates are produced. The structure is multilayer, consisting of 5 overlays, dried at 90 °C and post annealed at 180 °C for 3 minutes. The layer now is homogeneous, without cracks. The polymer solution was fluently overflowed and covered fully the substrate’s surface. This effect was emphasized from the smooth glass surface too. However, at silicon, as well as at glass substrates, the adhesion of the layer is still not enough strong. When scratch dried layers, after their post annealing treatment it can be seen its partially obliterating, because of the good wetting from the softened polymer which present here in form of thicker film (Fig. 5).

For increasing of the initial uniformity of the layers, spin coating method was used. The results are shown on Fig. 6, where picture a) corresponds to single layer, deposited on silicon wafer and annealed; picture b) corresponds to two annealed layers, deposited on same type of substrate and picture c) corresponds to the side
view of the interface between PVDF layer and the silicon substrate. The produced layers are thinner in comparison with those, obtained by casting method, and because of this, second deposition is necessary after first layer drying. The solvent evaporation time during the second deposition is longer than the penetration time of the solvent into the underlying coating. For this reason, before every subsequent covering, the previous layer must be hardened to avoid partially dissolving of the sublayers and throwing of the dissolved material under influence of the centrifugal forces.

Figure 6

3.2. Electrical characterization by using of surface acoustic wave (SAW) method

By using of sample, realizing surface acoustic method (SAW), it can be obtained information about the direct and reverse piezoelectric effect of given material and its sensitivity can be checked. In the present case, for the optimal conditions of PVDF layer deposition, the prepared samples are used to check, if the layer preserves or not its piezoelectric properties, which is the most important factor for good reaction of the future pressure sensing device. Metal layer from nickel-chrome alloy was made on glass substrate. By using of standard photolithography process, certain topology was created in this metallization. The topology represents 10 opposite to one another comb electrodes, each of them having width of 13.5 μm and distance in between of 15.5 μm (Figure 7). Two pairs of these electrode configurations were created in length of 32 mm and they were used like input and output transducers. The structure is planar and the piezopolymeric layer is obtained by 5 subsequent depositions and annealing at 180°C.
At the input of the transducer, sinusoidal signal with amplitude of 5.6 V and frequency, changing in the range between 350 Hz and 200 kHz, was applied. The output signals were observed with digital oscilloscope, which covers the investigated frequency range. The connections between the sample and the generator and oscilloscope were fixed by standard BNC connectors with connection impedance of 50 Ω. By decreasing of the input signal’s frequency, the amplitude of the output signal also decreases, which is connected with losses. The non-linear distortions in the output were also larger and the phase is shifted toward 90°. The shape, phase and amplitude of the both signals for the different frequencies can be seen on Figure 8 a), b) and c).

4. Conclusion

It was produced repeatable microstructure of the layers and it was found the optimal combination of deposition and post-deposition conditions for uniform full covering of the substrates. Although the necessity of high temperature treatment, the layers preserve their piezoelectric properties, which is proved by penetration of surface acoustic wave. The working frequency range, in which the losses and distortions of the output signal are acceptable, is between 3 kHz and 200 kHz.
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References