

Thin Film Microsensing Elements, Technology and Application in Microsystems for Environment Control

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Abstract. In this paper microsensing elements with thin piezoelectric films are presented. Three different materials from the basic types – ceramic, metal oxide and polymer, in microsystems for environment parameters control are used.

Zinc oxide (ZnO) and lead zirconium titanate (PZT) by sputtering technology from hot targets are deposited. The optimal parameters of the process and thickness of the layers are presented. Layers of piezoelectrical polymer poly (vinylidene fluoride) (PVDF) were prepared by spray deposition technique.

The microelements (MEMS) with these piezoelectric films are proposed for direct and indirect measuring of parameters as pressure, vibration, gas and liquid sensing, fluid flow, etc.

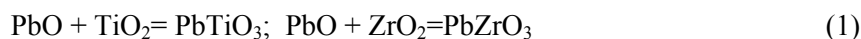
1. Introduction

The working principle of the piezoelements or structures is always in connection with the presence of a mechanical deformation, that leads to generation of charge carriers or in opposite, by applying a voltage to them, they are mechanically deformed, or a spatial motion of the structure could be observed. That processes are noticed in many MEMS structures and harvesting devices.

The use of the piezomaterials is in connection with the knowledge of their parameters, effects, properties and methods of deposition. The development of technologies and the synthesis of new materials allow successful implementation of structures with piezogenerating or sensitive functions in several electronic devices. New, widely used piezomaterials are: PVDF- organic polymer, PZT- piezoceramic, ZnO- metal oxide etc.

The recent data about poly (vinylidene fluoride) (PVDF), with piezo- and pyroelectrical properties, appears in the specialized literature [1]. The wide application of PVDF, as piezoelectric layers, in different pressure and force sensors and actuators is conditioned from its ability for low cost and simple methods of deposition onto standard substrates.

PZT is piezoelectric from the group of the piezoceramics that could be synthesized by two basic technologies. By the first of them, the corresponding titanates and zirconates are preliminary synthesized and after that mixed in suitable ratio, in order co-synthesis process of the specific component is possible from the solid solvents of PZT. The second technological sequence gives the possibility to produce materials with higher quality. The chemical reactions are given as the following:



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ZnO is amongst the most widely studied of all metal oxide systems and has recently become a very popular material. Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV) and one of the most widely used and studied functional oxides[2]. Zinc oxide readily forms into noncentral symmetric wurtzite nanocrystal structures with self-polarized crystal surfaces. Zinc oxide is desirable for many applications, such as piezoelectric transducers, varistors, gas sensors and transparent conducting thin films. ZnO is a key technological material. The lack of a center of symmetry in wurtzite phase, combined with strong electromechanical coupling, results in pronounced piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors.

The PZT, ZnO and PVDF layers were investigated by Fourier transform IR spectroscopy (FTIR).

2. Experimental

The PVDF can exist in several crystalline phases. From the five known modifications, the α - and β phases are stable and the most common. The β -phase is the desirable phase due to its piezo-, pyro- and ferroelectric characteristic. For deposition of PVDF layers by spray method, laboratory stand was designed (figure 1), which consists of adjustable flat heater with power 350 W, placed on dielectric ceramic substrate. The set temperature is controlled by electronic regulator. The temperature range which can be set is 30-120°C and the accuracy in this range is 2°C [3].

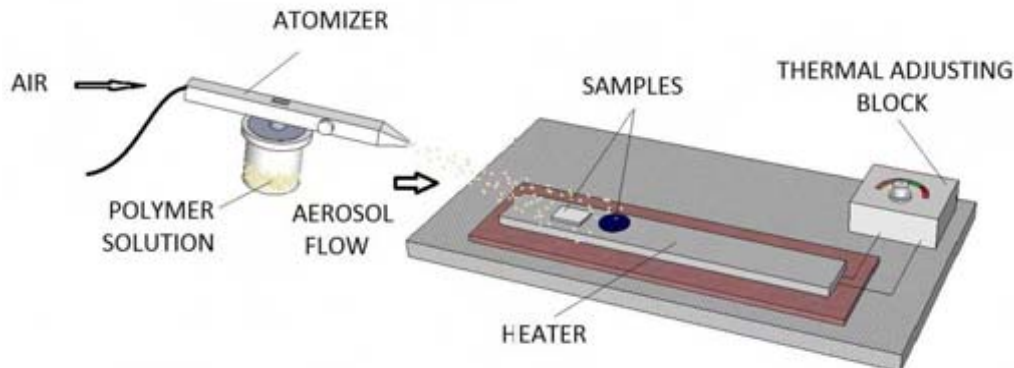


Figure 1. Experimental setup for the spray deposition of PVDF thin films.

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 methyl ethyl ketone (MEK).

For the deposition of thin PZT and ZnO layers, the sputtering targets of $(\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3)$ and ZnO with purity 99.99% were purchased from "Semiconductor Wafer, Inc." and "Goodfellow" with 75 mm diameter and 3 mm thick, respectively. PZT target was mounted in vacuum chamber of Leybold sputter coating system A400 VL.

The films were deposited by RF sputtering process. The exact deposition conditions were as follow: base vacuum 2×10^{-5} Torr, the gas partial pressure of Ar 2.5×10^{-2} Torr, sputtering voltage $U_{\text{plsm}} = 0.75$ kV, $I_{\text{plsm}} = 150$ mA, sputtering power $P_{\text{plsm}} = 112$ W. The growth rates are 2.5 nm/min for PZT and 9 nm/min ZnO, respectively [4].

For characterization of the layers, FTIR spectroscopy was applied with IRPresige 21 Shimadzu spectrophotometer in the spectral range of 350 cm^{-1} to 4000 cm^{-1} .

3. Results and discussion

3.1. PVDF layers

For further confirmation of the phases in the PVDF films, FTIR characterization was employed. The FTIR analyzing of layer were in reflectance mode and the measured spectrum is given in figure 2.

According to literature, the absorption peaks at 411 , 530 , 615 , 766 , 795 , 855 , 974 , 1149 , 1210 , 1383 , 1402 , 1432 and 1455 cm^{-1} can be used for α -phase identification [5, 6].

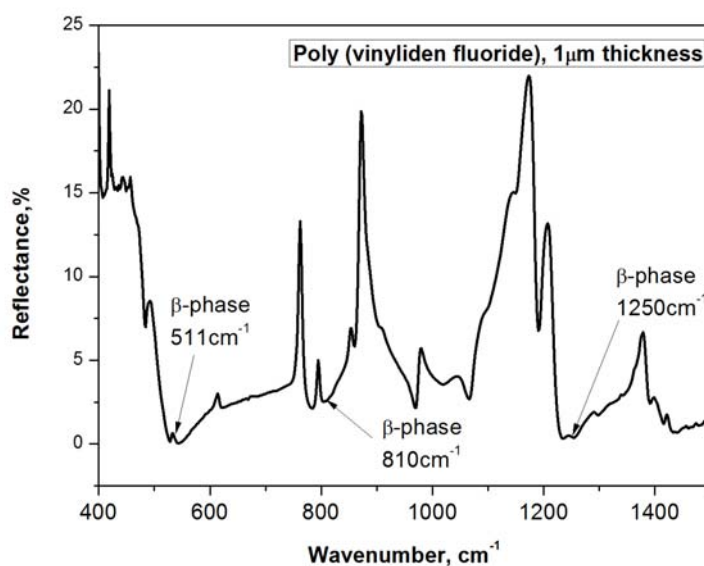


Figure 2. FTIR spectrum of sprayed PVDF film.

The detected peaks at 511 , 600 , 840 and 1275 cm^{-1} are the fingerprints of β -phase [5, 6]. The identified absorption bands are rich in information on the conformational isomerism of the chain, providing information for the β – phase presence. The characteristic bands related to the β - phase have been identified at 1250 , 810 and 511 cm^{-1} .

3.2. ZnO thin films

Infrared spectrum of ZnO films was obtained in reflectance mode in the spectral range of 350 to 1100 cm^{-1} (see figure 3). The absorption band at 390 cm^{-1} is usually reported for ZnO as a typical absorption feature [7].

The absorption peak at 406 cm^{-1} is theoretically confirmed for wurtzite zinc oxide as infrared active mode. The absorption band at 430 cm^{-1} is assigned to the stretching vibrations of Zn-O bond [8, 9], characteristic for ZnO. The IR lines at 560 and 814 cm^{-1} are due to the stretching vibrations of Zn-O bond [10].

FTIR analysis reveals that there is an indication of wurtzite crystal phase in the sputtered zinc oxide films.

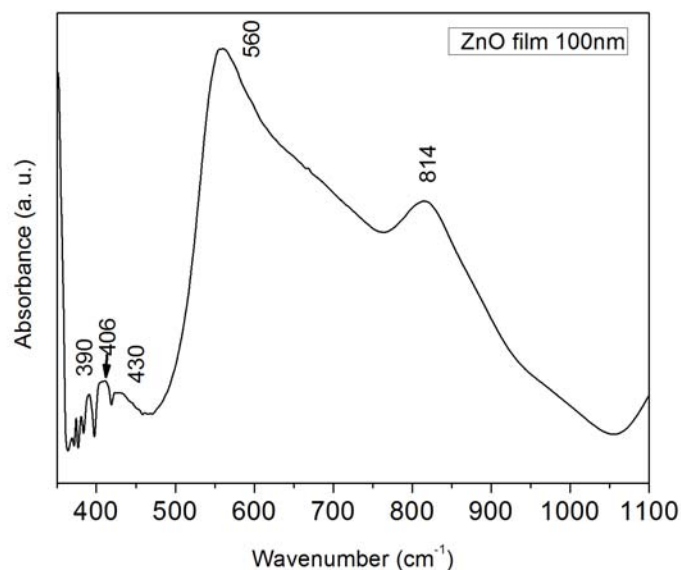


Figure 3. FTIR spectrum of sputtered ZnO film.

3.3. PZT thin films

PZT (and many other piezoelectric materials) have crystal structures belonging to the perovskite family with the general formula ABO_3 . It is known that the perovskite phase is the only desired crystal structure which has the ideal piezoelectric properties. FTIR spectroscopy as a very sensitive tool can give some information for the chemical bondings and structure of the studied samples.

FTIR spectrum of PZT thin film in reflectance mode is presented in figure 4. The bands appear in the range of from 450 to 350 cm^{-1} are related to B–O vibrations (BO_6 and B–O for ABO_3 structures) [11, 12]. The instinctive feature at 550 cm^{-1} is observed. This band resembles with the reported FTIR observations of PZT ceramics [13].

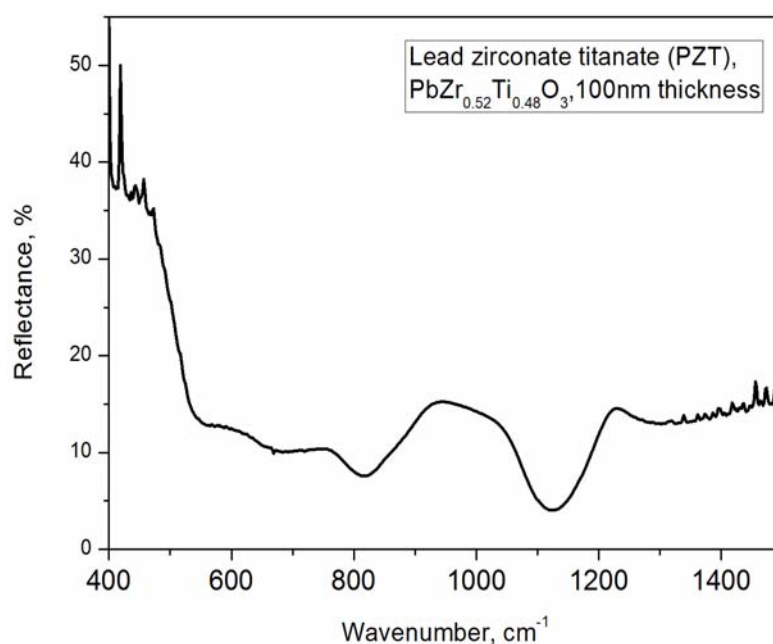


Figure 4. FTIR spectrum of sputtered PZT film.

In this spectral area, a broad band can be seen from 800 to 550 cm^{-1} with a maximum at 780 cm^{-1} . [10] This peak has been associated with the vibration of M–O (M = Zr or Ti) bonds in the systems.

The FTIR results confirm the formation of perovskite phase of lead zirconium titanate. This is a promising result as it manifests that PZT films in perovskite crystal structure can be deposited by RF sputtering process and respectively this is a favorable phase structure for exhibiting good piezoelectric properties.

3.4. Application of the studied films

Many MEMS sensors working with small motion of thin film structures use piezoelectric layers as gas (SAW), pressure, flow sensors, etc. The films in these devices have to possess piezoelectric properties, which are observed by forward and reverse effect. Some typical applications are shown in figure 5.

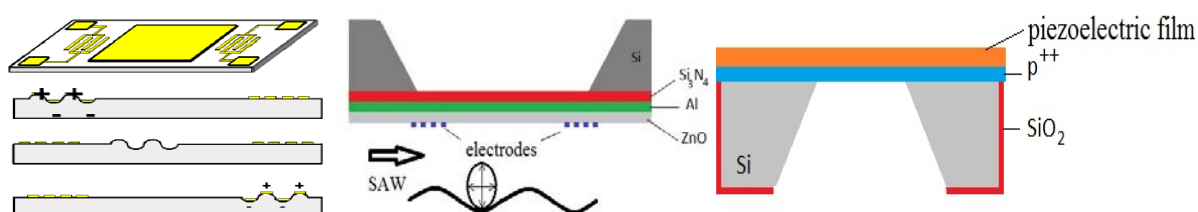


Figure 5. Examples of typical applications of thin piezoelectric films.

4. Conclusion

The layer of PVDF- MEK solution was deposited by spray technology at optimal process parameters. The obtained PVDF films were investigated by FTIR spectroscopy and it was found that the organic solvent MEK contributes for the crystallization of PVDF films in polar β - phase.

Thin films of PZT and ZnO were deposited by RF sputtering process. The FTIR spectrum shows that the perovskite phase is formed in PZT layers by revealing characteristic infrared modes. FTIR spectrum of ZnO film shows the absorption bands that are indicative for wurtzite zinc oxide crystal phase.

The main conclusion that can be drawn from this investigation is that the thin films of PVDF, PZT and ZnO can be successful candidates as piezoelectric layers in MEMS devices, sensors and actuators for environment control.

Acknowledgment

This paper was presented at INERA Workshop "Transition Metal Oxide Thin Films-functional Layers in "Smart Windows" and Water Splitting Devices", September 4-6th, 2014, Varna, Bulgaria. The Workshop is part of the Program of INERA REGPOT Project of Institute of Solid State Physics, Bulgarian Academy of Sciences.

The authors are thankful to Assoc. Prof. Dr Tatyana Ivanova (Central Laboratory of Solar Energy and New Energy Sources at the Bulgarian Academy of Science) for the measurements of FTIR spectra.

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