Some metal oxides and their applications for creation of Microsystems (MEMS) and Energy Harvesting Devices (EHD)

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Abstract. This is a review of a part of the work of the Technological Design Group at Technical University of Sofia, Faculty of Electronic Engineering and Technologies, Department of Microelectronics. It is dealing with piezoelectric polymer materials and their application in different microsystems (MEMS) and Energy Harvesting Devices (EHD), some organic materials and their application in organic (OLED) displays, some transparent conductive materials etc. The metal oxides Lead Zirconium Titanate (PZT) and Zinc Oxide (ZnO) are used as piezoelectric layers - driving part of different sensors, actuators and EHD. These materials are studied in term of their performance in dependence on the deposition conditions and parameters. They were deposited as thin films by using RF Sputtering System. As technological substrates, glass plates and Polyethylenetherephtalate (PET) foils were used. For characterization of the materials, a test structure, based on Surface Acoustic Waves (SAW), was designed and prepared. The layers were characterized by Fourier Transform Infrared spectroscopy (FTIR). The piezoelectric response was tested at variety of mechanical loads (tensile strain, stress) in static and dynamic (multiple bending) mode. The single-layered and double-layered structures were prepared for piezoelectric efficiency increase. A structure of piezoelectric energy transformer is proposed and investigated.

1. Introduction

Nowadays, the energy resources on the Earth are near to their depletion. For this reason, more attention has been started to pay to so called renewable energy sources and harvesting devices, to the decreasing of the power, consumed from various electronic devices, and to devices, having their own, autonomous power supply [1]. Many low power electronic devices, like clocks, portable radios, CD players, mobile telephones etc., have additional energy source, besides the battery supply [2]. The newly developed materials and the effects, related to them, play a key role to the design and the manufacturing of such type of devices.

Many microelectronic devices are used for generation of electricity, transducing different type of energy. It is related to the usage of specific materials, whose properties and effects provide electric charges, when mechanical stress or force is applied to them [3].

Piezoelectric effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress. One of the unique characteristics of the piezoelectric effect is that it is reversible, meaning that materials, exhibiting the direct piezoelectric effect (generation of electricity, when stress is applied) exhibit the converse piezoelectric effect as well (generation of stress, when an electric field is applied) [4]. This effect is observed in crystals that have no center of symmetry. Some of the most popular materials, that possess piezoelectric properties, are lead zirconate titanate (Pb(Zr,Ti)O$_3$ or PZT), zinc oxide (ZnO), aluminum nitrate (AlN) etc. [5]. They show piezoelectric effect with different piezoelectric coefficients. The application of the piezomaterials is related to the knowledge of their parameters and the methods, used for their deposition [6].
Some ceramic materials have dielectric constants, which are up to 100 times higher than those of the ordinary crystals. These synthetic materials are classified in a new group, that of ferroelectrics. They have piezoelectric constants much higher than that of the natural materials. This leads to intensive investigations for synthesizing of materials like PZT, which have favourable piezoelectric parameters, as well as that of zinc oxide (ZnO) [7].

Piezoelectric materials, such as PZT and ZnO are very important for the Micro-electro-mechanical systems (MEMS) and Nano-electro-mechanical systems (NEMS) design, as sensors and actuators. Traditionally, the PZT and ZnO are used as bulk materials, with thickness, higher than 100-200 μm. The requirements for miniaturization can be fulfilled by conversion of the piezoelectric materials into thin nanometric films, via using of some of the conventional microelectronic technologies, like RF sputtering.

2. Physical parameters of PZT and ZnO

Actually, PZT is piezoelectric ceramic, for which, the proportion between zirconium and titanium (Zr/Ti) is defined for certain specific application. There could be seen variety of compositions, but the most frequently used are 54/46; 52/48; 50/50; 53/47; 80/20 etc. PZT is a ferroelectric material which has excellent piezoelectric and pyroelectric properties. [8]. The synthesis of Pb(Zr,Ti)O₃ is rather complicated. The technological processes are carried out in tightly closed containers or capsules at high temperatures [9]. It should be mentioned that, the most of the available ceramics, such as PZT, are based on the structure of perovskite (figure 1). Usually, the typical thickness of the piezoelectric PZT layers in MEMS technologies is in the same range as that of ZnO layers - 0.05-3 μm [10].

![Figure 1. Perovskite structure of PZT.](image)

The most important coefficients, related to piezoelectric films, and their values, typical for PZT nanometric films, are as follows:

- Piezoelectric coefficients (Strain) \( d_{31} = 180.10^{-12} \text{C/N} \); \( d_{33} = 360.10^{-12} \text{C/N} \);
- Piezoelectric coefficients (Voltage) \( g_{31} = 0.011 \text{V/m/N} \); \( g_{33} = 0.025 \text{V/m/N} \);
- Coefficient of electromechanical transformation \( k = 0.35-0.69 \);
- Elasticity modulus \( Y = 49-63 \text{GPa} \);
- Relative dielectric permittivity \( \varepsilon_r = 1700 \);
- Curie temperature \( T_C = 330-360^\circ\text{C} \) [11].

ZnO or zinc oxide forms a hexagonal wurtzite structure with lattice constants \( a = 3.25 \text{ Å} \) and \( c = 5.2 \text{ Å} \). It possesses the lack of center of symmetry, required for piezoelectric materials (figure 2). The piezoelectric coefficients for ZnO are also relatively high, which makes it an excellent material to be used in a wide variety of piezoelectric applications [12]. Besides in MEMS, they are used also in optoelectronics, in mobile communications for different kinds of filters, using surface acoustic waves and for thin film resonators for bulk acoustic waves. They are used also as chemical sensors.

The coefficient of electromechanical transformation of ZnO has relatively high value, which makes it an excellent material for large number of piezoelectric systems (MEMS, sensors and actuators). The properties of zinc oxide coatings depend on the method and parameters of deposition. RF Sputtering is
the most frequently used deposition method due to the uniform thickness of the produced layer and because of the fact that it could be applied on different type of substrates.

![Hexagonal crystal structure of ZnO.](image)

The typical values of the piezoelectric coefficients for ZnO nanometric films are as follows:

- Piezoelectric coefficients (Strain) \( d_{31} = 5.10^{-12} \text{ C/N}; \ d_{33} = 12.4, 10^{-12} \text{ C/N}; \)
- Piezoelectric coefficients (Voltage) \( g_{31} = 0.36 \text{ Vm/N}; \ g_{33} = 1.57 \text{ Vm/N}; \)
- Coefficient of electromechanical transformation \( k = 0.33 \) [13];
- Elasticity modulus \( Y = 30-200 \text{ GPa}; \)
- Relative dielectric permittivity \( \varepsilon_r = 10-11 \)

3. Experimental work on PZT and ZnO layers deposition, their characterization and measurement of the SAW test structures

In our work these basic materials are used like thin films, with thickness of around x.100 nm. As a result the piezoelectric response is weaker, comparing to bulk material. Several groups of experiments were done with the aims, firstly, to estimate the quality and to determine the parameters of PZT and ZnO layers and on the second place, to define the proper deposition procedures for optimization of the layers’ piezoelectric response. The films were deposited by using a RF Sputtering System. More details about the concrete deposition conditions can be found elsewhere [6, 8, 10]. For investigation of the films, a Surface Acoustic Wave (SAW) structure was prepared (figure 3), by using of which, the piezoelectric effects in the two materials, can be easily detected.

![Top view of a SAW structure.](image)

The structure consists of two pairs of comb electrodes, which are the input and output transducers, respectively. They were prepared by using of chrome layer, deposited on glass substrate and patterned by photolithography. The both samples (PZT and ZnO) were prepared with the same mask configuration and dimensions. The layers of piezoelectric material were deposited on top and between the electrodes. The aim is, by making of the input transducer to vibrate, a mechanical wave in the piezoelectric material to be generated. The vibration is excited by sinusoidal signal, provided by a functional generator (MPF3060, 60MHz) at certain frequencies. When a mechanical wave was generated, it was spread into the whole piezoelectric layer, deposited on the electrodes and the area between them. The wave induces a voltage between the electrodes, when it reaches the output
transducer. By dual channel oscilloscope (DQ2041CN), the signals of the structure’s input and output were observed simultaneously. In figure 4, the curves of ZnO and PZT reactions are shown [14].

Because of the low elasticity of the glass substrate we cannot estimate the exact electromechanical coupling coefficients. This is the reason, the mechanical waves, induced by the input transducer to be restricted in their magnitude. As a consequence, the amplitude of the output voltage was also limited, but the results of 17 mV for ZnO and 10mV for PZT from peak to peak at input signal parameters 200kHz and 9Vp-p is quite good result for this film piezoelectric structure. The conclusion is that there is a coupling between the input and output transducers of the SAW structure, because of the presence of the piezoelectric materials. Moreover, the structure may serve as piezotransformer, as the output signal remains with sinusoidal shape with negligible distortions and no shift at the higher frequency (figure 4).

For better elasticity, a flexible organic substrate of polyethylenetherephtalate (PET) was used. In figure 5, a simplified technological sequence and the cross-section view of the structure is shown. For the top and bottom electrodes, Al layers, with thickness of 200 nm, were used. For the proposed structure, a piezoelectric material PZT, with a thickness of about ~150 nm and piezoelectric coefficient $d_{33}=360$ pC/N was used. By this approach, a bigger amplitude of the output voltage, in comparison to

![Diagram of Voltage generated by the PZT and ZnO based SAW structures](image)

**Figure 4.** Voltage generated by the PZT and ZnO based SAW structures [14].
the ZnO ($d_{33}=12.4 \text{ pC/N}$), was achieved.

![Figure 5. Technological sequence of microgenerator](image)

For mechanical testing of the piezoelectric microgenerator in dynamic mode, the setup, presented in figure 6, was used. As a mechanical wave source an electromagnetic shaker was used. It consists of a coil with an anchor, at the end of which the sample is clipped. The coil was supplied by sinusoidal voltage with defined frequency. During the mechanical vibration of the structure, a voltage with almost the same sinusoidal shape was generated. The measurement was performed by using of a digital oscilloscope, whose two channels, were connected respectively to the sample and to the coil. Figure 7 represents the dependence of the generated voltage on the electrode’s area, respectively for 100 Hz and 200 Hz. As can be seen, the increase of the electrodes area and the vibration frequency increases the output power of the generator, because of the fact that the flexible substrate provides higher elasticity of the whole structure, which ensures the corresponding voltage generation, by using of lower mechanical loading.

![Figure 6. Measurement setup for dynamic mode testing.](image)

![Figure 7. Dependence of the generated voltage versus the electrode’s area at different activation frequencies.](image)

In one of the studies of 180 nm PZT layers on flexible PET substrate, the effect of the aluminum electrodes configuration on the generated voltage at static stress was investigated. Both types of fabricated structures are shown in figure 8. Testing conditions and schematic view of the test setup for voltage-stress characteristic measurements can be found elsewhere [6]. The first one is sandwich type with top and bottom aluminum electrodes, deposited by thermal evaporation. The second configuration consists of PET substrate, layer PZT on it and finally – several top electrodes, laterally patterned.

In the case of the sandwich type structure (figure 8a), the sensor is not sensitive to mechanical stress, lower than 100 mg (figure 9). Possible reason for this lack of sensitivity, to weak stress, is the fact that the orientation and polarization of PZT particles, for this type of structure, are predominantly
in lateral direction. As a result, the piezoelectric reaction is hard to be detected, with vertical loading of the electrodes. That’s why a lateral structure was produced (figure 8b) and tested (figure 10).

**Figure 8.** Cross section of the PZT piezoelectric sensor. a) sandwich type; b) lateral type [6].

**Figure 9.** Voltage-stress dependence for the sandwich type structure [6].

**Figure 10.** Voltage-stress dependence for the lateral type structure [6].

The piezoelectric coefficient, generating charge in direction, perpendicular to the applied stress, could be described by the equation [15]:

\[
d_{31} = 2\varepsilon_0\varepsilon_r P_r Q_{12},
\]

where \(P_r\) is the voltage, measured during the experiment, \(\varepsilon_r\) is PZT dielectric permittivity (\(\varepsilon_r = 1700\)), \(\varepsilon_0\) is dielectric constant in vacuum (\(\varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m}\)) and \(Q_{12}\) is the electrostrictive coefficient, or the ability of the dielectric materials to reorient the electrical domains inside the material. After calculations, for this coefficient, it was obtained value of \(d_{31} = 186 \text{ pC/N}\). For comparison, the maximal value of this coefficient, for PZT-layers, deposited from solution, is 78 \text{ pC/N}. This result can be explained by the better PZT layer morphology here. For the samples with planar electrodes, the sensitivity is higher than the values, obtained from the sandwich type structure and the voltage-stress characteristic is highly linear. The main reason is probably the fact that, during PZT deposition, the polarization is directed perpendicularly to the applied stress \((d_{31})\) [10]. In this case the charge is generated between two neighboring electrodes and can be easily measured. The sensor has relatively wide dynamic range, in which the linearity deviation is only 1.8 %.

The electrical parameters and reaction of PZT sensors with planar electrodes are quite similar and even higher than those, given in other publications. The eventual reasons for the good efficiency are:
1) the flexible substrate, providing higher mechanical deformation than silicon wafer, and 2) suitable deposition rate of sputtered PZT layers, allowing to the particles to take more favorable energetic positions and to build up proper crystal lattice with preliminary defined piezoelectric properties.

The next set of experiments was conducted to check and prove the microstructure and the state of the chemical bonds in the layers. For this reason, FTIR spectroscopy was applied with IRPresige 21 Shimadzu spectrophotometer in the spectral range of 350 cm$^{-1}$ to 4000 cm$^{-1}$. FTIR spectroscopy as a very sensitive tool can give some information for the chemical bondings and structure of the studied samples.

The Infrared spectrum of ZnO films was obtained in reflectance mode in the spectral range of 350 to 1100 cm$^{-1}$ (see figure 11). The absorption band at 390 cm$^{-1}$ is usually reported for ZnO as a typical absorption feature [16]. 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 [17, 18], which is characteristic for ZnO. The IR lines at 560 and 814 cm$^{-1}$ are also due to the stretching vibrations of Zn-O bond [19].

PZT 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 spectrum of PZT thin film, in reflectance mode, is presented in figure 12. The bands appearing in the range of 450 to 350 cm$^{-1}$ are related to B–O vibrations (BO$_6$ and B–O for ABO$_3$ structures) [20, 21]. The distinctive feature at 550 cm$^{-1}$ is observed. This band resembles the reported FTIR observations of PZT ceramics [22]. In this spectral area, a broad band can be seen from 800 to 550 cm$^{-1}$ with a maximum at 780 cm$^{-1}$. This peak has been associated with the vibration of M–O (M = Zr or Ti) bonds in the systems.

The obtained FTIR results confirmed the formation of piezoelectric phase of ZnO and PZT. This is a promising result, as it manifests, that both films can be deposited by RF sputtering process and respectively these are favorable phase structures for exhibiting good piezoelectric properties.

4. Study of double-layer piezoelectric structures based on PZT and ZnO.

This section presents the study of double-layer flexible piezoelectric structures, containing combination of PZT and ZnO single-layers in different order of deposition in relation to the near substrate criteria. Firstly, PZT was deposited on the PET, covered by Al, covered as a second layer of ZnO, and vice versa. The aim of this study was fabrication of piezoelectric transformers. For comparison data about the single layered structures are given. Oscillograms of the signal produced are presented in figures 13 and 14 [24].
For the single layer configuration the voltage, generated from the 200 nm thick PZT layer was in the range 40-60 mV. The values of 40 mV were measured at 23 Hz and 33 Hz and the values of 60 mV at 45 Hz and 55 Hz. At the same measuring conditions, the generated voltage, taken from the single-layer piezoelectric structure of ZnO was in the range 80-100 mV - 80 mV was measured at 23 Hz, 45 Hz and 55 Hz and 100 mV, was measured at 33 Hz.

For the double layered structure with first layer of PZT and second ZnO, the generated piezoelectric voltage is almost a half of that, obtained from the previous one-layer structures. Its value is in the range 30-40 mV, and only at higher frequencies, values of 80 mV were monitored. For 45 Hz and 55 Hz measuring points, due to depolarization or inability of the dipoles of both materials to follow the changes of the mechanical load with the same speed, the PZT layer cannot produce a charge. This behavior is probably due to the increased inner capacitance of the double layered structure.

In figure 13 some of the signals of the generated piezoelectric voltage, obtained from the structures are presented.

![Figure 13](a) ![Figure 13](b)

**Figure 13.** Output voltage signals of the double-layer structure with PZT and ZnO layers for different frequencies [24].

For the second type of double layer structure, the first deposited material was ZnO and the second one - PZT. Like in the previous case, the value of generated piezoelectric voltage is almost a half of that for the single-layer structures. Here, at 23 Hz and 33 Hz, the voltage is around 40 mV and at 45 Hz and 55 Hz some values of 80-100 mV were rarely observed. Some signals, of the piezoelectric voltage, which is generated by this double-layer structure, are shown in figure 14.

![Figure 14](a) ![Figure 14](b)

**Figure 14.** Output voltage signals of the double-layer structure with ZnO and PZT [24].
After considering the generated piezoelectric voltage signals of all structures, it could be concluded that both two-layer structures have a lower output voltage. They actually generate a higher charge, but the inner capacitance is bigger and, as a result, the output measured voltage is lower. For one-layer structures, more interesting is the fact that the 60 nm ZnO layer has almost the same voltage values as the voltage, obtained by the 200 nm PZT layer. This could be a consequence of the piezoelectric coefficients of the layers. Another fact is that, the value of the output voltage, at 23 Hz and 33 Hz, for single-layer samples, is lower but for two-layer sample is higher. At higher frequencies, it is just in opposite, but future work should be done to clarify the processes occurred.

5. Conclusion
Based on the experiments it could be said that the PZT and ZnO based thin film devices can be successfully applied as piezoelectric stress sensors, energy harvesters and piezoelectric transformers. Piezoelectric sensor structures, using sputtered PZT layers, operate in different ranges of the applied stress, depending on the electrodes configuration. Using of flexible PET substrate provides higher elasticity of the piezostructure, which increases the voltage generation, even at lower mechanical loading and makes the energy harvesting devices more sensitive and effective. After considering the generated piezoelectric voltage signals of all structures, it could be concluded that, two-layer structure have a lower output voltage and can be used as piezoelectric decreasing transformers.

Acknowledgements: This paper was presented at INERA Conference „Vapor Phase Technologies for Metal Oxide and Carbon Nanostructures“, 5-9 July, 2016, Velingrad, Bulgaria. The Conference is part of the Program of INERA REGPOT Project of Institute of Solid State Physics, Bulgarian Academy of Sciences.

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