

# Atomic force microscopy investigation of piezoelectric response of ZnO thin films deposited by HIPIMS

V. TIRON\*, T. COMAN, L. SIRGHI, G. POPA

"Alexandru Ioan Cuza" University of Iasi, Faculty of Physics, Blvd. Carol I, No. 11, 700506, Iasi, Romania

This work reports the effects of substrate temperature and the pressure of the deposition gas on the crystal quality and piezoelectric response of zinc oxide thin films deposited by High Power Impulse Magnetron Sputtering (HIPIMS). The effects of substrate temperature and gas pressure on piezoelectric property of the deposited ZnO films were investigated locally (with nanoscale resolution) by Piezoelectric Force Microscopy (PFM) in connection with the film structure, which was investigated by X-ray diffraction), and the film surface morphology, which was investigated by Atomic Force Microscopy (AFM). Deposition temperature and gas pressure have a strong effect on the piezoelectric response and crystallinity of the thin layers in terms of grain size, residual strain and surface roughness. Piezoelectric response and crystallinity of ZnO were improved considerably by decreasing the gas pressure and/or by increasing substrate temperature. The PFM images reveal that the ZnO films have inversion domains and pronounced grain boundaries.

(Received September 25, 2012; accepted February 20, 2013)

**Keywords:** Zinc oxide, Magnetron sputtering, Piezoelectric properties

## 1. Introduction

In recent years, there has been an increased interest in ZnO thin films due to their potential applications as piezoelectric films for surface acoustic wave devices (SAW), microsensors, microactuators and acousto-optic devices [1]. Films with highly piezoelectric properties and good photoluminescence response are prime candidates to fabricate UV sensors based on surface acoustic wave devices [2, 3]. Piezoelectric materials for SAW devices must possess favorable *c*-axis properties for preferred growth, for a high electromechanical coupling coefficient, as well as high resistivity for low insertion loss and little distortion of the frequency response [4].

Thin film properties are highly dependent on the deposition parameters like type and energy of deposited species, film bombardment, and nature and temperature of the substrate. These parameters control a number of processes as surface heating, enhancement of atomic mobility, displacement of lattice atoms, creation of lattice defects, recoil implantation of surface atoms into the substrate layer and sputter desorption of contaminant species. These processes determine the mesostructure, grain size, surface morphology, micro-strain and residual stress of the deposited films. In the case of the sputter deposition, the transport of the atoms to the substrate is controlled by working gas pressure and geometry of reactor chamber, while diffusion of add atoms in the film is controlled mostly by the substrate temperature, which may be significantly influenced by energetic particles bombardment.

The aim of the present research is to investigate the influence of substrate temperature and gas pressure on the crystal quality and piezoelectric response of zinc oxide thin films deposited by High Power Impulse Magnetron Sputtering (HIPIMS). The structural properties and piezoelectric response of the deposited films were

investigated using X-ray diffraction, atomic force microscopy (AFM) and piezoelectric measurements.

## 2. Experiment

ZnO thin films were deposited on Ti/SiO<sub>2</sub>-Si (100) wafers by high power impulse magnetron sputtering method using a zinc target (99.99% purity, circular shape, 56 mm in diameter) in an oxygen and argon gas mixture. The ratio of oxygen to argon was ¼ and the target-substrate distance was 60 mm.

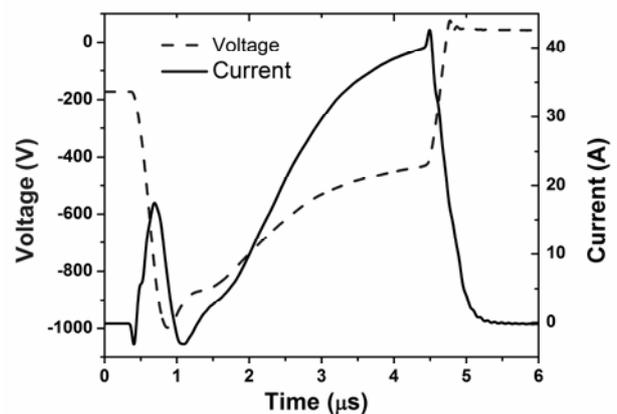


Fig. 1. Typical variation of discharge voltage and current intensity during one discharge pulse.

The reactive pulsed magnetron discharge operates in a preionised regime (pulse width: 4  $\mu$ s, repetition pulse frequency: 1 - 5 kHz, target voltage: up to 1 kV, current density: 1-10 A/cm<sup>2</sup>). Typical variation of discharge voltage and current intensity during one discharge pulse is shown in Fig. 1. The repetition frequency of high-voltage

pulses was 1 kHz, the pulse duration was 4  $\mu$ s, the gas pressure was 50 mTorr and the average power on discharge was 80 W.

By proper preionisation is possible to reduce the breakdown delay to work in very short pulse regime (1-10  $\mu$ s), so that electric arcs are avoided. This preionization discharge current assures impulses in discharge current intensity with the amplitude as large as 40 A. The pulsed reactive magnetron discharge operates with lower breakdown delay, high ion-to-neutral flux ratio at the substrate, no arc development and provides very good sputtering process stability, without hysteresis effect [5]. The most important advantage of the HIPIMS is high ionization rate of sputtered material and the resulting higher mobility of the species adsorbed on the substrate which is beneficial for coatings with crystalline structure.

The silicon wafers used in this work were cleaned in an ultrasonic bath of acetone and ethanol during 15 minutes, rinsed in deionized water, and subsequently dried with flowing nitrogen. In order to perform piezoelectric measurements, the silicon substrates were covered with a thin titanium layer using the same deposition system with a titanium target and argon as working gas. We choose the titanium layer as bottom electrode because of the small lattice mismatch between the ZnO and titanium, which enables growth of films with higher crystal order. The titanium deposition parameters were: gas pressure - 10 mTorr, pulse width - 4  $\mu$ s, repetition pulse frequency - 4 kHz, target voltage - 0.9 kV and average power - 90 W, target to substrate distance - 60 mm and deposition time - 10 minutes. Before starting the ZnO deposition process, the zinc target was presputtered for 10 min in order to remove any contaminant from its surface and reach stable conditions.

The crystalline quality and crystal orientation of deposited ZnO thin films were investigated by an X-ray diffraction apparatus (LabX XRD-6000 from Shimadzu Co.) using Cu K $\alpha$  X-ray source, in configuration  $\theta$ - $2\theta$ .

Surface morphology, roughness, grain size and piezoelectric force microscopy (PFM) images were determined using a multimode AFM setup (NT-MDT SolvePro). PFM was employed to investigate the local electromechanical (piezoelectric) properties of the ZnO films. Essentially, PFM is based on the detection of the local electromechanical vibration of the sample caused by an external alternating current (AC) voltage. The voltage is applied to a conductive (platinum covered) AFM probing tip, which is used as a movable top electrode. The external driving voltage with frequency  $\nu$  generates a sample surface vibration with the same frequency due to the converse piezoelectric effect. The modulated deflection signal from the cantilever, which oscillates together with the sample, is detected using the lock-in technique. The amplitude of the first harmonic signal from the lock-in amplifier is a function of the magnitude of piezoelectric displacement and phase shift between the AC electric field and the cantilever displacement [6]. Thus, during AFM scanning of the sample surface the magnitude of the AFM tip displacement is recorded simultaneously with the phase of the displacement (orientation of the piezoelectric response). This means that regions with opposite piezoelectric orientation will vibrate in counter phase with respect to each other under the applied electric

field, and hence appear as regions of strong contrast in the phase image [7]. The Pt/Ir coated cantilevers with a typical tip radius of 10 nm, spring constant 0.06 N/m and resonant frequency of 200 kHz were used at a scan rate of 0.5 Hz. An AC signal  $V_{ac} = V_0 \sin(\omega t)$  with amplitude 1 V and frequency 150 kHz was applied between the AFM tip (movable top electrode) and the bottom electrode of the sample to acquire the PFM images with the aid of the lock-in amplifier.

### 3. Results and discussion

#### 3.1 Effect of the gas pressure on the crystal quality and piezoelectric response

In order to investigate the influence of gas pressure on the crystal quality and piezoelectric response, several samples of zinc oxide thin films were deposited at different gas pressures maintaining the same average power (80 W) and the same deposition time (1/2 h). During film growth, the deposition temperature was maintained at 200  $^{\circ}$ C. The substrate temperature was monitored using a thermocouple placed near the substrate. Fig. 2 shows the XRD patterns of these samples deposited at several values of gas pressure in the reactive plasma. The XRD patterns show that ZnO thin films are polycrystalline and the intensity of the diffraction peaks is decreasing with the increasing the gas pressure. The presence of a diffraction peak around  $34^{\circ}$  corresponds to the c-axis oriented ZnO crystal growth along the (002) crystal plane. This c-axis crystal orientation is essential in providing useful piezoelectric properties for devices. Therefore, zinc oxide films exhibit high piezoelectric response when the crystallites have the c-axis perpendicular to the substrate.

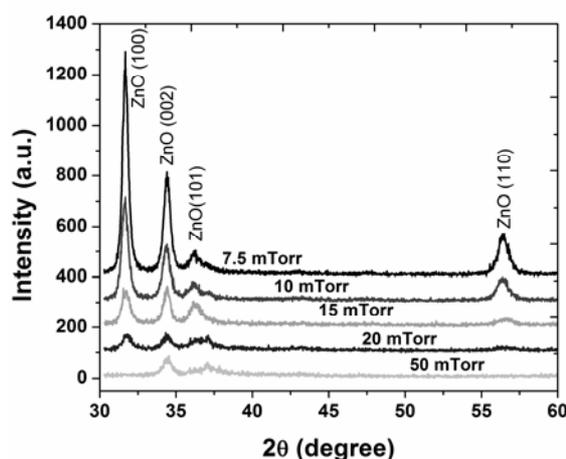


Fig. 2. XRD patterns of ZnO thin films deposited at different gas pressures.

There are three deposition parameters with dominant influence on the ZnO crystal quality: the oxygen content of the working gas, energetic ion bombardment and substrate temperature. If the oxygen partial pressure is too low, the films are grown with an oxygen-deficiency and a deviation from a high c-axis orientated crystal can occur.

At low gas pressure the free mean path of the sputtered particles is large and energy of the particles which arrive at the substrate is high. The intense bombardment in depositions at low gas pressure improves the crystal

quality of the deposited thin films. Besides these important growth parameters, there is an influence of substrate temperature, which can improve also the crystal quality and preferred nucleation.

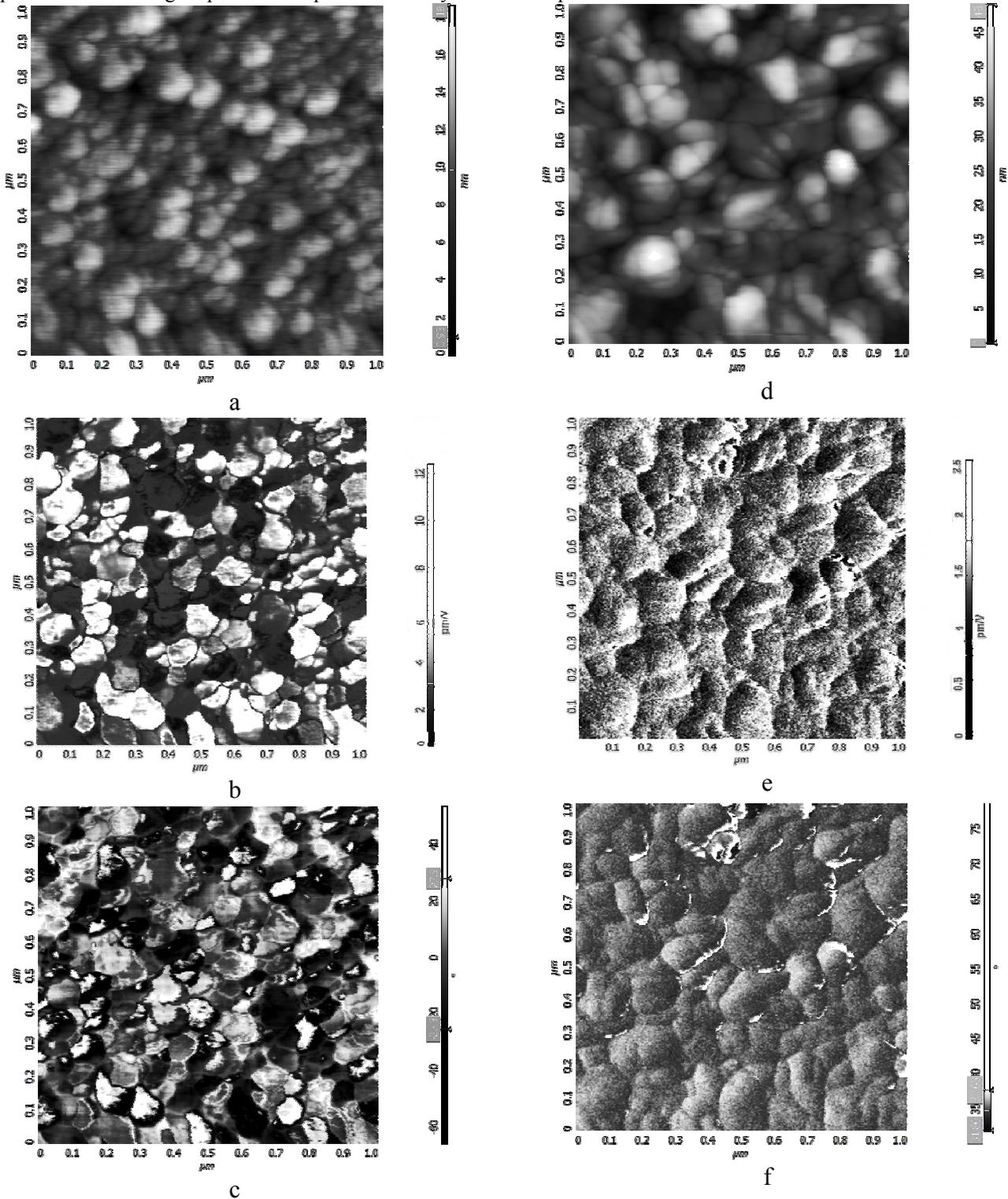


Fig. 3. Topography (a,d), PFM magnitude (b,e) and phase (c,f) of ZnO film sputtered on Ti/SiO<sub>2</sub>-Si (100) wafers by high power impulse magnetron sputtering at 7.5 mTorr (left side) and 50 mTorr (right side) gas pressure.

In order to understand the factors that influence the piezoelectric properties and to optimize material properties, it is important to determine the quantitatively the piezoelectricity of the deposited films. The principal performance-determining parameter for piezoelectric materials is called  $d_{33}$  - the piezoelectric coefficient. It indicates the charge per unit force in the polarization direction of the sample when the electric field and the strain are both along the polarization axis.

Fig. 3 illustrates a set of typical PFM images ( $1 \times 1 \mu\text{m}^2$  size) for the ZnO films sputtered on Ti/SiO<sub>2</sub>-Si (100) substrates by high power impulse magnetron sputtering at 7.5 mTorr and 50 mTorr. Fig. 3 shows the topography (a,d), the magnitude of the piezoelectric response (b,e) and the phase image (c,f). In Fig. 3b, the bright regions indicate those grains (or cluster of grains) with high piezoresponse or  $d_{33}$  constant while the dark regions indicate a low piezoelectric response. The imaged samples show a variety of contrasts implying a spread in the local  $d_{33}$  values. A point worth mentioning is that not all regions are vibrating in phase with the applied signal. In Fig. 3c, the bright images represent regions of the surface that are vibrating in phase with respect to the driving voltage. The ZnO crystallizes in the wurtzite structure, and thus does not possess inversion symmetry. This lack of inversion symmetry leads to polarity effects, particularly along the [0001] direction, which results in a net dipole moment along the [0001] direction. It is possible that these oppositely directed vibrations arise from regions of the sample where the polarization is also opposed and thus the contrasts observed in these PFM images could strongly be related to polarity effects [8]. The bright and dark regions are called "inversion domains" where the polarities are completely opposite to each other. The PFM images of ZnO thin films have a nonuniform magnitude and phase contrast. The PFM magnitude image can be used to quantify the piezoelectric response because it possesses information about the local piezoelectric coefficients of the imaged sample. The force curve when the probe is tapping on the sample is used to determine the amplitude sensitivity, which calibrates the magnitude signal (nA) into pm/V.

The intensity of piezoelectric response is higher for the film deposited at lower pressure (12.4 pm/V at 7.5 mTorr and 2.5 pm/V for film deposited at 50 mTorr). ZnO has a  $d_{33}$  piezoelectric coefficient that can vary depending on the quality of the film and the orientation of the crystals. Similar results ( $d_{33} = 12.4$  pm/V) was also reported by the Rosenbaum [9], which means that for every volt that is applied on sample the surface displacement will be only 12.4 picometers. The grain boundaries are more pronounced in deposited thin films at lower gas pressure. The grain boundaries are zones where surplus oxygen atoms are located, which are highly insulating and therefore prevent charge carriers transfer between individual grains [10]. Films with pronounced grain boundaries seem to promote the piezoelectric properties.

The average values of piezoelectric response were measured from magnitude images of films deposited at

different values of gas pressure. Fig. 4 shows the average piezoelectric response and average roughness of the ZnO thin films deposited under different working gas pressures. The average piezoelectric response is much larger for samples deposited at low pressure. This is in agreement with the XRD measurements (Fig.2), which indicate a better crystallinity at lower gas pressure. The samples with higher intensity (002) peaks and lower FWHM values have the best piezoelectric response because of their excellent crystalline quality. The presence of the inversion domain is due to the lack of preferential crystal orientation.

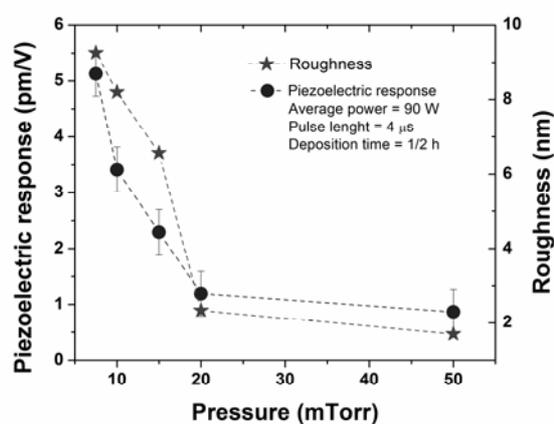


Fig. 4. Piezoelectric response and roughness of ZnO thin films deposited at different gas pressures.

The surface roughness, measured from AFM topography, decreases from 9.26 nm to 2.34 nm quickly, when pressure increases from 7.5 mTorr to 20 mTorr and then continues to decrease slightly to 1.7 nm. This can be explained by diffusion processes. Since at higher pressures the deposition rate decreases, the atoms reaching the surface have more time for surface diffusion. This results in a lower density of nucleation centers. Another possible explanation is the reduced bombardment with energetic particles at higher pressures, which leads to a decreased roughness of the growing film.

### 3.2 Effect of the substrate temperature on the crystal quality and piezoelectric response

In order to investigate the influence substrate temperature on the crystal quality and piezoelectric response of zinc oxide thin films, ZnO thin films were deposited at different substrate temperature maintaining the same average power (80 W) and the same deposition time (1/2 h). During film growth, the gas pressure was 50 mTorr. Fig. 5 shows the XRD patterns of these samples deposited at different substrate temperature in reactive plasma. By increasing the substrate temperature, the overall atomic mobility increases leading to ZnO (002) preferred orientation along  $c$ -axis, as it is shown by the XRD measurements. The intensity of the (002) peak

increases with the deposition temperature, which indicates improving crystallinity and preferential orientation of the thin films. The full-width at half-maximum (FWHM) of the diffraction peak continues to decrease at higher deposition temperature.

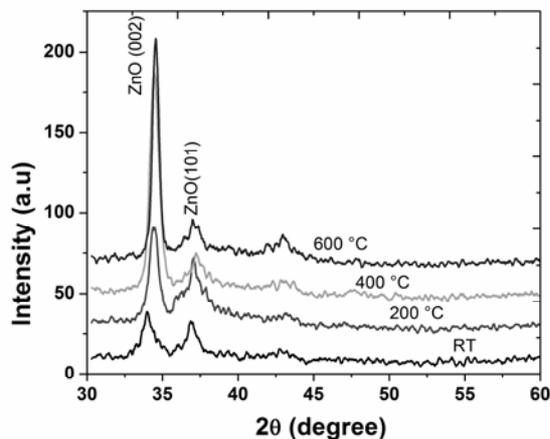


Fig. 5. XRD patterns of ZnO thin films deposited at different substrate temperatures.

The diffraction angle of the (002) peak increases from  $34^\circ$  to  $34.56^\circ$  with the substrate temperature increasing from room temperature (RT) to  $600^\circ\text{C}$ , due to relaxation of the films. The shift of the ZnO (002) diffraction peak's location to lower angles values results from the residual stress and strain in ZnO crystal lattices caused by the deposition process [11].

In Fig. 6 is illustrated the influence of the deposition temperature on the average piezoelectric response of the ZnO thin films. The piezoelectric response was improved by increasing the substrate temperature, but is lower than in case of ZnO films deposited at low gas pressure. The energy of the bombarding particles has a stronger influence on the piezoelectric response.

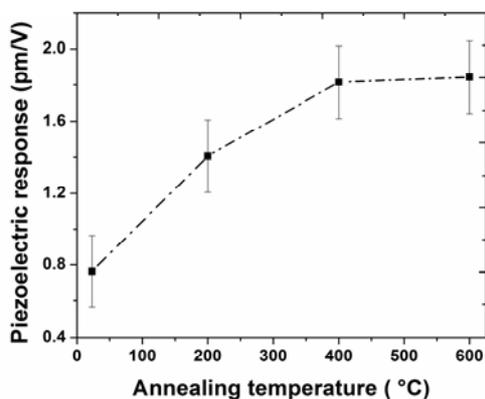


Fig. 6. Piezoelectric response of ZnO thin films deposited at different substrate temperatures.

## 4 Conclusions

In this paper, PFM, which is based on the AFM technique, was employed to investigate the local electromechanical (piezoelectric) properties of the ZnO thin films deposited by high power impulse magnetron sputtering at various values of working gas pressure and substrate temperature.

It was found that deposited ZnO thin films yielded better crystal quality and piezoelectric response at low gas pressure and high substrate temperature, as evident by XRD analysis and PFM measurements, respectively.

The PFM measurements reveal that the ZnO films have a complex domain structure with inversion domains and pronounced grain boundaries. The presence of the inversion domain is due to the lack of preferential crystal orientation.

## Acknowledgments

This work was supported by the European Social Fund in Romania, under the responsibility of the Managing Authority for the Sectoral Operational Programme for Human Resources Development 2007-2013 (grant POSDRU/89/1.5/S/49944).

## References

- [1] E.S. Kim, R.S. Muller, IC-Processed Piezoelectric Microphone, *IEEE Electron. Dev. Lett.* **8**, 467 (1987).
- [2] K. Liu, M. Sakurai, M. Aono, *Sensors* **10**, 8604 (2010).
- [3] L.P. Schuler, M.M. Alkaiasi, P. Miller, R.J. Reeves, *Microelectron. Eng.* **83**, 1403 (2006).
- [4] J.-B. Lee, H.-J. Lee, S.-H. Seo, J.-S. Park, *Thin Solid Films* **398–399**, 641 (2001).
- [5] M. Ganciu, M. Hecq, S. Konstantinidis, J. P. Dauchot, M. Touzeau, L. dePouques, J. Bretagne, *European Patent Appl. No. 4447072.2 / 22.03.2004*.
- [6] S.V. Kalinin, A. Gruverman, *Scanning Probe Microscopy of Electrical and Electromechanical Phenomena at the Nanoscale*, Springer (2006).
- [7] A. Gruverman, S.V. Kalinin, *J. Mater. Sci.* **41**, 107 (2006).
- [8] L.P. Schuler, N. Valanoor, P. Miller, I. Guy, R.J. Reeves, M.M. Alkaiasi, *Journal of Electronic Materials* **36**, 507 (2007).
- [9] J. F. Rosenbaum, *Bulk Acoustic Wave Theory and Devices*, Norwood, MA: Artech House Inc., 1945.
- [10] Van de Krol, R. and H.L. Tuller, *Solid State Ionics* **150**, 167 (2002).
- [11] D.-S. Liu et al., *Japanese Journal of Applied Physics* **45**, 3531 (2006).

\* Corresponding author: vasiletiron@yahoo.co.uk