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Nanostructured PZT type thin films prepared by thermionic vacuum arc method

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PZT type films were prepared using the thermionic vacuum arc (TVA) method; a crucible filled PZT type powder (PbO/ZrO/TiO) was heated by a thermo-electron beam emitted by the circular cathode of the TVA gun. Applying high voltage potential (3000 ± 200V) on the anode from a regulated HEINZINGER high voltage power supply the thermo-electrons were accelerated toward the anode crucible, evaporating the anode materials and initiating a plasma discharge. The morphology and the structure of the prepared films analyzed by transmission electron microscopy, (TEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy, showed nanostructured, smooth thin films with specific PZT stoichiometry.

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1. Introduction

PZT is a perovskite crystalline ceramics. Perovskite structure is adopted by many oxides which have the chemical formula ABO_3 . The structure is adaptable and has many applications. PZT is composed by the lead, zirconium and titanium, with the formula: $Pb[Zr_xTi_{1-x}]O_3$, where $0 < x < 1$. The most common chemical compound is $PbZ_{0,52}Ti_{0,48}O_3$. There are known many deposition methods for PZT type piezoelectric thin film materials: vacuum cathode sputtering of sintered powder and thermionic vacuum arc being two of them. This paper proposes the use of thermionic vacuum arc method [a-d] with the purpose of the production of the PZT thin film deposit. The deposits of this method may occur only under the circumstances of high and ultrahigh vacuum (residual pressure must be under 10^{-6} torr). It is used a specially outside heated cathode in order to ensure a powerful electronic thermoemission.

In the recent years, perovskite oxide thin films have become one of the most studied materials, due for their widely applications in the microelectronic and optoelectronic devices, including nonvolatile feroelectric memories, piezolelctric microactuators and sensors, optical waweguides and microwave devices. Among many types of of perovskite thin films, lead zirconate titanate (PZT) is being intensively studied due to its large remanent polarization and relatively high Curie temperature.Typically, submicron films are deposited onto various oxide single crystal substrates, such as MgO[1], $SrTiO_3$[2], $LaAlO_3$ [3], $LaNiO_3$[4] and onto Pt/Ti/SiO_2/Si substrates using a sputtering technique[5,6,7].

2. Experimental

The material that needs to be evaporated is put in a graphite (black lead) caster located at a few millimeter far from the cathode. On the cathode it is applied a positive voltage of 1-6 KV, depending on the material that needs to de deposited and on the conditions in which the deposit process takes place. The external heating process of the cathode is done and that is why the lighting up process of the arc and it's maintaining can be done at 0.3 A and at anodic voltage of over few hundreds of V, even kV. Limiting the discharge current is done with the balast resistance from the circuit's exterior. Thus it is reached the usual discharge in vacuum arc. By the current's exterior heating process of the cathode and of the voltage applied to the anode some small current plasmas and high tensions may be generated exclusively in the anode material. Thus, the substrates is located in vacuum, and on it the evaporated material deposits both under the form of atoms and of ions. The measurements done have shown that the energy of the ions that arrive on the surface may vary between 100 and 900 eV, depending on the heating of the cathode and on the voltage applied to the anode. The ionic current at the substracte surface may be of the μA order, depending on the same parameters. By the method developed by us, the atoms deposed on the substrate are extracted from the anode by electrons bombardment, the electrons' mass being much smaller than the ions' one it is expected to be extracted from the anode especially atoms and not large groups. The existence of an ionic bombardment of the status in formation process is benefic for its adherence and compactness. In this case, the ions are of the same nature with the material that needs to be deposed and have high enough energies and intensities for their acceleration towards the surface. Due to the thickness of the prepared films that is of the hundred of nm order, and to the deposit speeds that are of some nm/s order, the duration of the deposit is of the minute order, which makes a possible heating of the surface, due to the thermal radiation of the TVA arc plasma, could be negligible, and the film integrity will not be affected during the deposition. The reaction chamber is cylindrical, having a volume of about 800 l. The access port is located in the front side of the deposition system. This is provided with a monitoring system of the thickness of the film during the deposition working on the principle of the quartz balance crystal. The chamber is provided with a number of flanges to which may be attached the isolated or mechanical entries (for linear movements or rotations of the elements from the chamber). The side parts of the chamber have some stainless steel pipes attached which allow the activating of a water cooling or heating system. The anterior part of the chamber opens completely. It is provided with two circular windows through which one can view the phenomena from the inside of the chamber. The windows are protected by applying on the inferior part some glass screens of appropriate diameter. For ignition and maintaining the TVA arc are necessary two circuits: one for the heating of the cathode filament, where a relatively low voltage source (0-24V) provides a 10-150 A current and another one that is designed for the running up of the arc discharge, being used for this an adjustable source of high voltage (0-4 kV) and a current up to 3 A.

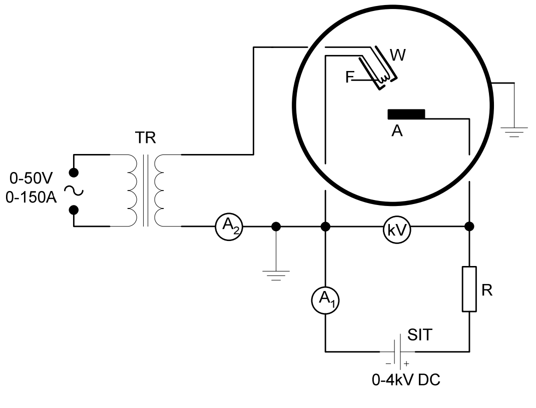


Fig.1.Electric Scheme of the experimental set-up.

The vacuum chamber and the cathode are connected by ground. The ampermeters and voltmeter are necessary to monitor the power of the TVA arc during the film deposition. If the breakdown conditions are accomplished, applying a high tension between the heated cathode and the anode, in the space between the electrodes appears a bright discharge, extremely stable as far as the shape, the value of the discharge current and the emitted light intensity are concerned. From the moment of applying the voltage up to the apparition of the discharge it is necessary a time in which the anode material to melt, and then it begins to evaporate up to the settling of a stationary density of the anode material vapors in the inter-electrode space. Once with the ignition of the TVA arc, it will occur volume expansion of the plasma of the anode material vapors, the plasma having a density which will decrease with the distance (r) towards the crucible which contains the melted material. The number of the evaporated particles from a source of punctual evaporation which fall in the unit from the surface unit of the surface is in inverse ratio to the square of the distance from the source to the surface. The whole quantity of evaporated material in a second towards all the directions from the surface if the source is m* (g/s) then the the dm* material quantity which passes through a solid angle $dw = ds \cdot \cos\theta / r^2$ is given by the relation :

$$dm^* = \frac{\left(\frac{m^*}{4\pi}\right) \cdot \cos\theta \cdot ds}{r^2} \quad (1),$$

which is Knudsen-Lambert law relation.

where: ds is the elementary surface on which the deposition is done, θ - the incidental angle at the ds surface. In the TVA arc, the cathodic fall reaches values of the kV order. This is due to the fact that for the starting the breakdown process, the voltage must, on one hand ensure the production of a sufficient number of electric charge carriers, and on the other hand, ensure the generation of the gas in which the discharge through an appropriate atom vapors density is produced. After the ignition of the discharge the distribution of the potential is set in the inter-electrodic space, the cathode fall having a much bigger value than in the case of the usual electric arc. The electron emission from the cathode is independent from the parameters of the TVA arc plasma. If the cathode – anode distance increases (for example due to the evaporation of the anode material), in order to maintain the electron current which comes from the cathode to the anode, the accelerating voltage must be raised which leads to the raising of the cathode fall. If the TVA electronic gun is inclined to an angle from which the anode is “seen” at a smaller solid angle, for collecting the same electron’ current, we must raise the cathode fall. After the ignition of the TVA arc, the stable maintaining of the discharge requires a continuous generations, with a constant rate, of the anode material vapors. This is accomplished by the dissipated power at the anode, which is equal with the product between the anode fall and the intensity of the arc current:

$$P_a = U_a \cdot I_{arc} \quad (2)$$

The expansion of the plasma is produced on the walls of the chamber, the vapors’ density according to Knudsen-Lambert law, from the anode on the radial direction. Next to the anode, the elementary processes that determine the expansion of the plasma are the collisions determined by the coulumb forces, and also by the collisions between the isolated atoms and those through which the charge transfer takes place. The balance of the charge carriers is equilibrated on one hand by the losses determined by the bipolar ambipolar transport and by the reactions in volume, and on the other hand, the main production process of the electric charges is the electronic impact. During the expansion of the plasma from the anode, the atoms' and the ions' densities decrease. The bipolar ambipolar transport of electrons and the number of ions determine an electric field which slows the electrons and accelerates the ions. In the anode plasma's interior the transfer collisions have an important role in the ions' transport. At small distances towards the anode of approximately 10 nm, only the Coulumbien collisions influence the charge transfer towards the electrodes. For bigger distances, the plasma is expanded without the collisions. As far as the potential is concerned, the difference between the interelectrode plasma and the metallic chamber is equal to the cathode decrease, because the chamber and the cathode are tied to the ground. The ions produced in the plasma will end up on the chamber's walls with energy equally proportional with the cathode decrease. This one is influenced by the geometric and optional factors: the intercathode distance (d), the relative position of the electrodes given by the φ angle and the cathode temperature determined by the intensity of the heating current of the filament(I_f).

The total decrease of tension on the arc U_{arc} is given by:

$$U_{arc} = U_c + U_{pl} + U_a \tag{3}$$

where Uc- the tension decrease on the cathode: U_{pl}- the plasma total decrease; U_a- the tension decrease on the anode.. U_a has such a value that the generation process of the atoms from the anode must be maintained at the same level with the one before the lighting up of the arc, which means:

$$\mathrm{U_a} \cdot \mathrm{I_{arc}} = \mathrm{I} \cdot \mathrm{U_s} \tag{4}$$

where I_{arc}- the intensity of the current that passes through the arc: U_s- the puncture intensity; I- the intensity of the current before the lighting up process of the discharge on the U_{pl} plasma potential. The plasma's conductivity is big so as the cathode decrease can be neglected in comparison with the other values of the potential decreases on the anode and the cathode. The stability of the discharge is an important characteristic of the TVA method. The TVA arc plasma's peculiarities may be resumed: a pure web in the evaporated material's vapors in the nacelle of the anode; the ionization degree is high due to high plasma density; the ions' energy is stable; the cathode decrease reaches the kV level; the arc parameters adjustment may be done only modifying the operations' conditions(I_f, U_a, I_a).

The PZT thin films deposits were done on different surfaces: silicon plates with the following sizes: 20 mm x 20mm x 0.5 mm, specially covered with a thin film-platinum electrode, glass plates with the following dimensions 8 mm x 80 mm x 1 mm, ceramics plates with the dimensions 15 mm x 15 mm x 0.5 mm. The surfaces were positioned in the TVA deposition device on specially manufactured holders, at 300-400 mm distance from the TVA gun.

A mobile screen from stainless steel has been used, and the TVA parameters have been set. The deposition chamber has been under a residual pressure of 3×10^{-6} Torr before the beginning of the coatings. For plasma ignition, the TVA gun filament has been heated with a 40 A current and at an alternative voltage of 20 V. The continuous voltage has been applied on the anode with an increasing rate of approximately 1000 V/ min, being followed by the focusing process of the electron beam by a Wehnelt cylinder on the anode crucible.

When the powder in the crucible has melt, the applied voltage was adjusted in order to ensure the ignition of the discharge in the vapors of the PZT material. A stable discharge has been obtained at U_a=1200 V and I_a=300 mA. After checking the discharge stability the mobile screen was removed and the deposition started. The thickness of the film has been measured during the deposition with a Cressington equipment, which uses the quartz oscillators. The deposition has been interrupted when the indicated thickness was of 100 nm. After termination of the deposition, the anode voltage and the applied current to the TVA gun filament have been reduced to zero. The samples have been kept in the deposition chamber, under high vacuum for about 120 minutes, for the chamber's and substrate's temperature to cool down.

Fig.2.TVA anodic sistem set-up.

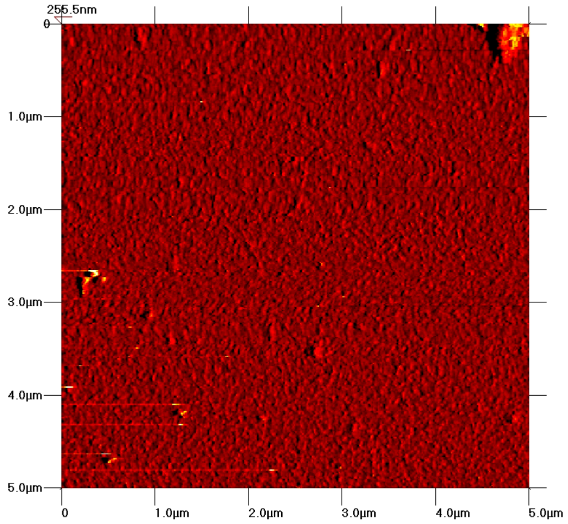
The XPS measurements were recorded with a VG ESCA III MK2 spectrometer system equipped with a monocromated Al kα X-ray source. High Resolution XPS Spectrum for C(1s), O(1s) and Pb(4f) signals of two PZT probes deposited onto ceramics were measured, over a binding energy range of 0-600eV, with pass energy of 100eV and 150eV for each of the probe.

Transmission Electron Microscopy (TEM) analysis were carried out by Philips CM120ST microscope, operating at 100kV with Cs = 1,2mm and ≈2 Å resolution.

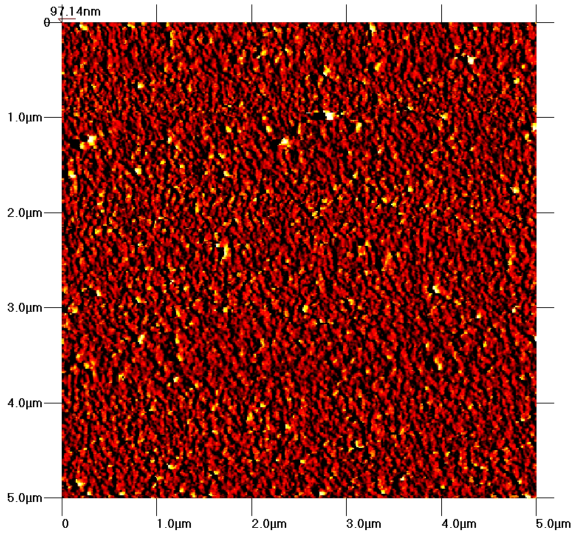
3. Results and discussions

AFM images for two probes of the PZT thin films deposited onto ceramic substrate (Fig.3) reveals that the thin film is well crystallized and craks free, and has nearly uniform grain distribution.The same caracteristics were founded by Z.Bi et al.[8] for PZT thin films deposited onto SiO_2/Si substrates using a RF- magnetron sputtering technique.

The average roughness R_a calculated for the AFM micrographs from fig.3 has the value of 100nm ± 10nm.



a) PZT2

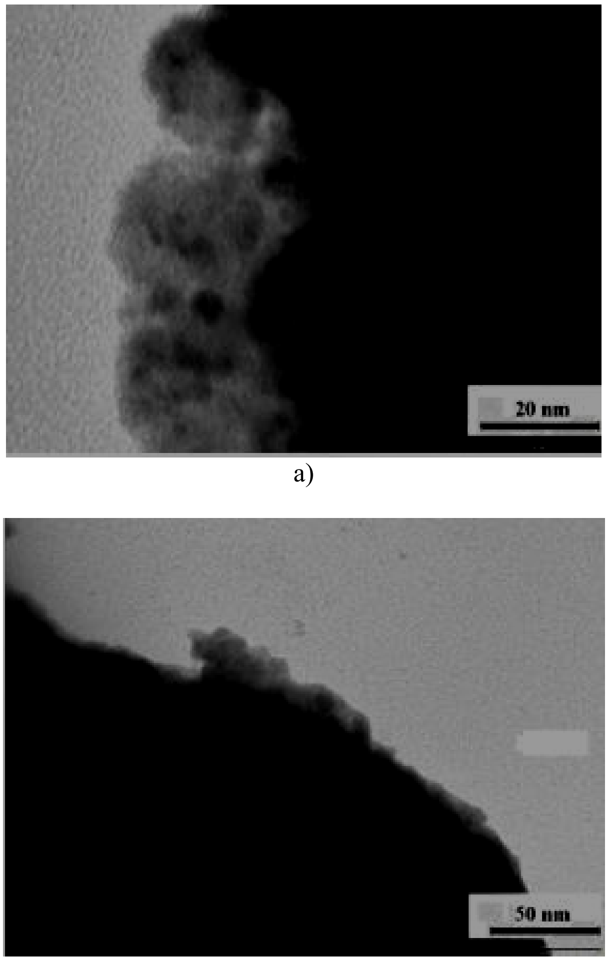


b)PZT3

Fig.3. AFM micrographs of the PZT probe on ceramic substrate.

J. Zhao et al.[9] showed that the AFM images of (001) textured PZT films on SiO_2/Si substrates present a structure with close-packed round-shaped particles having a homogenous size distribution and RMS roughness of 5nm.

From the TEM images of a probe analysed in this paper (Fig.4) we can observe that the grains have an average size of about 5-10 nm.



a)

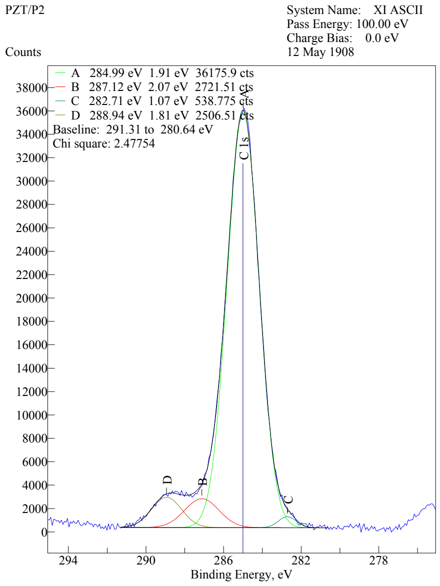
b)

Fig.4.TEM image of a PZT film.

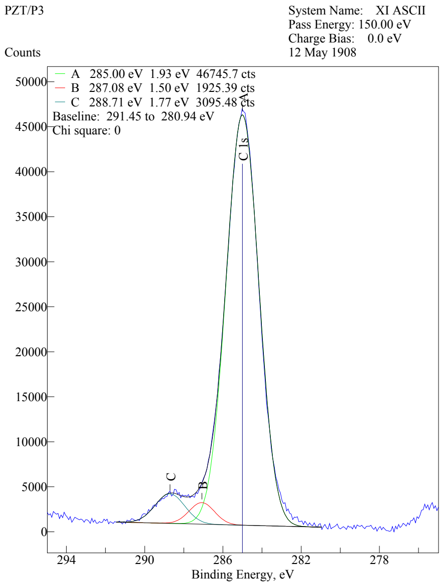
In this paper, XPS is used to study the oxidation states of the constituent atoms, especially oxigen in PZT thin films.

The aproximate composition of the film can be determined by dividing the individual peak areas (the most intense only), by their respective atomic sensitivity factor(ASF)[10].

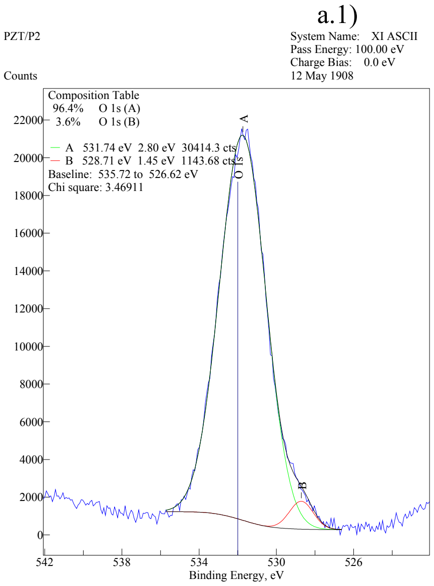
In fig.5 are presented the XPS spectra signals of the constituent atoms from PZT probe.



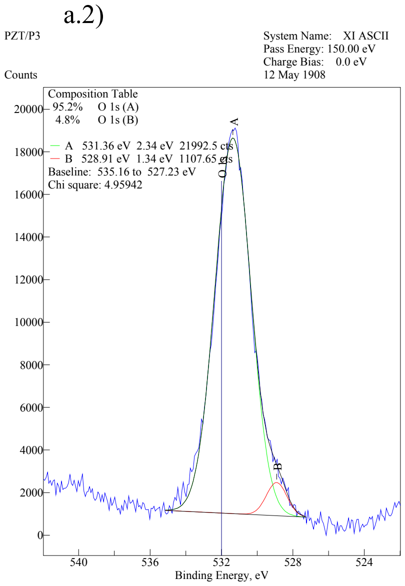
a.1)



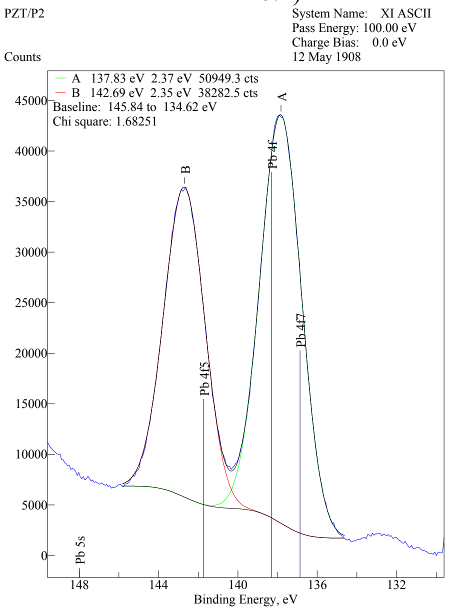
a.2)



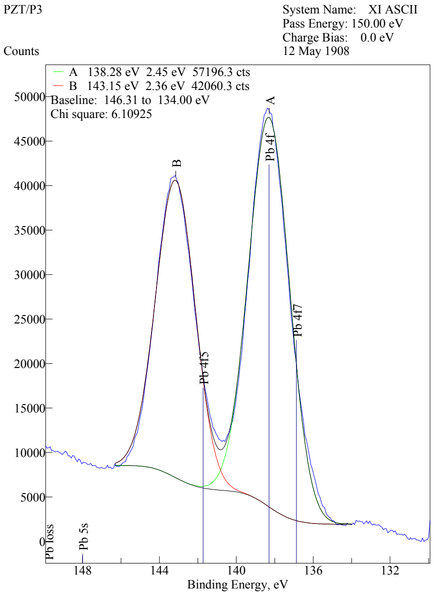
b.1)



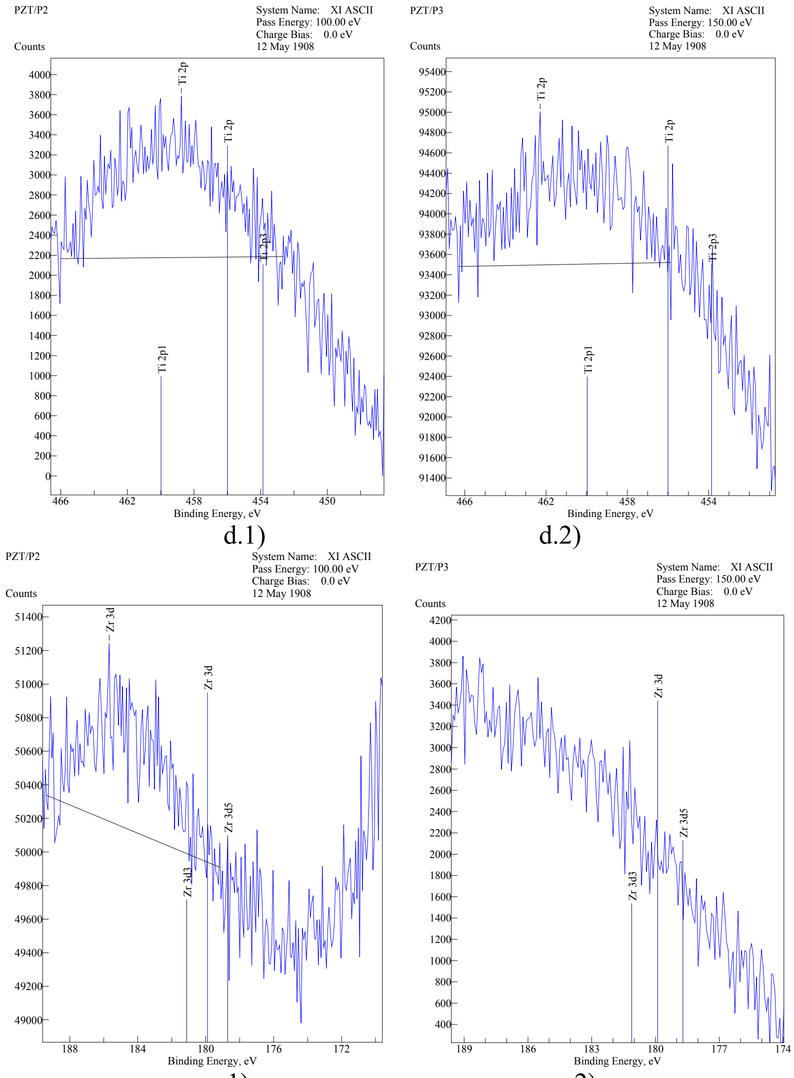
b.2)



c.1)



c.2)



d.1) d.2)

e.1) e.2)

Fig.5. High resolution XPS spectrum for: C(1s) signal – (a), O(1s) signal - (b), Pb(4f) signal – (c) and XPS spectral signals of Ti(2p) - (d) , Zr(2p) – (e) measured for two probes of PZT deposited onto ceramic substrates.Shifting was corrected using the C(1s) component ,with binding energy of 290eV.

The measured areas under Pb(4f) and O(1s) most intense peaks for PZT/P2 and PZT/P3 probes (in fig.5.b,5.c) are 50949 units and 57196 units,respectively for Pb(4f) peaks , 30414 units and 21992 units, respectively for O(1s) peak.

So, for the PZT/P2 probe we identify the stoichiometry of PbO(O/Pb units ratio □ 1), and for PZT/P3 probe we found the stoichiometry of Pb_2O_3 (O/Pb units ratio □ 1,3).

From fig.4.c we see that the O(1s) peaks have a small full width at half maximum(FWHM) value of about 1,9eV.

By comparation with standard ESCA spectra of Pb and line energy information [10], we can say that the Pb(4f) peaks at 137,8eV and 142,6eV are Pb^{4+} states in Pb_3O_4, while the Pb(4f) peaks at 138,2eV and 143,1eV are Pb^{2+} states in PbO.

The Ti(2p3/2) peak at 458,5eV localized in XPS signal spectra of Ti(2p) from fig.5.d.1) indicate Ti^{4+} oxidation state in TiO_2 , and the Ti(2p3/2) peak at 453,8eV showed in fig.5.d.2) indicate Ti^{2+} state in PZT[11].

The Zr(3d3/2) peak at 185,3eV for XPS signal of Zr(3d) from fig.5.e.1) indicate Zr^{4+} state in ZrO_2[12], and the Zr(3d3/2) peak at 181,1eV from fig.5.e.2) is Zr^{2+} in PZT.

4. Conclusions

The PbO/ZrO/TiO powder mixtures have been successively deposited onto different substrates using the PZT thin films TVA method.

The AFM measurements showed a small roughness of the films, and the TEM images indicate a nanometric dimension of the granules.

From the XPS analyses of the PZT thin films obtained on ceramics substrate we identified the formation of composites such as PbO_x, TiO_x, ZrO_x during the thin films growing process.

The future measurements will elucidate the cristalline structure of our PZT films and we will study the electrical parameters of those thin films.

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