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Structural, ferroelectric and dielectric properties of In_2O_3:Sn (ITO) on $PbZr_{0.53}Ti_{0.47}O_3$ (PZT)/Pt and annealing effect

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ABSTRACT

Ferroelectric indium tin oxide (ITO) on $PbZr_{0.53}Ti_{0.47}O_3$ (PZT)/Pt structure, prepared by RF sputtering onto SiO_2/Si substrates, is studied in order to investigate the effect of ITO as a top electrode in these systems. X-ray diffraction, scanning electron microscopy (SEM) and atomic force microscopy (AFM) experiments were performed to study the structure and the surface morphology of the samples. From X-ray diffraction, we observe that the ITO thin film grows with the (1 1 1) texture and the peaks attributed to PZT are all from the perovskite phase. The average roughness (RMS) of the PZT surface is found to be 1.650 nm from AFM experiment. The ferroelectric and dielectric properties were inferred from polarization hysteresis loops, capacitance and dielectric constant measurements. These properties have been compared to those of the widely studied Pt/PZT/Pt system prepared under the same conditions. The effect of ITO/PZT/Pt annealing has been studied. Annealing at 400 °C leads to 13% increase in the dielectric constant ε_r.
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1. Introduction

Ferroelectric thin films have been the subject of a lot of studies in recent years because of their practical and potential application in electronic devices, such as non volatile memories, infrared sensors, electro-optic modulators and micro-actuators [1–3]. One of the most studied films is the lead zirconate titanate, $PbZr_{0.53}Ti_{0.47}O_3$, commonly called PZT. Physical properties of Pt/PZT/Pt structures were also extensively investigated [4]. Recently, interest has been shifted to the Pt/PZT/ITO structures, i.e. the use of ITO as a bottom electrode [5,6]. In_2O_3:Sn (ITO) thin films are chosen for the very low electrical resistivity, high infrared reflectivity and high UV absorption [7]. Rao et al. [8] studied the ITO/PZT/ITO structure where ITO is used for both electrodes, they observed a high remnant polarization and better fatigue resistance in such a system. In a recent work, Yoom et al. [9] prepared lanthanum modified lead zirconate titanate (PLZT) onto ITO/glass substrate by RF magnetron sputtering method, they observed that annealing led to high remnant polarization values and good ferroelectricity and fatigue properties. Also, Hwang et al. [10] prepared PZT on Pt/ITO/glass by RF magnetron sputtering, i.e. a double bottom electrode and they used Pd as a top electrode; the authors showed that the use of Pt/ITO double bottom electrode improve the crystallization and the hysteresis behaviours compared to the Pt bottom electrode.

In the present work, we have investigated the physical properties of RF sputtered ITO/PZT/Pt structure, i.e. the use of ITO as a top electrode and compared these properties to those of the widely studied Pt/PZT/Pt system. Experimental methods are described in Section 2. In Section 3, we discuss the structure and the morphology of the ITO/PZT/Pt as well as the ferroelectric and dielectric properties of the ITO/PZT/Pt and Pt/PZT/Pt systems. The effect of annealing of the ITO/PZT/Pt structure is also reported in Section 3.

2. Experimental methods

The PZT thin films have been prepared by RF sputtering on Pt/Ti bilayer deposited onto SiO_2/Si substrates. The as-deposited films are amorphous. Annealing, in air for 1 h at 625 °C, leads to the crystallization of the PZT films with the correct chemical composition. The ITO film was deposited by RF sputtering from a ceramic In_2O_3:Sn target (90:10 wt.% 99.99) on the PZT/Ti/Pt structure. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) experiments were performed to study the surface and the interfaces (cross section images). X-ray diffraction (XRD) experiment, in the θ–2θ mode, was used to study the structure of the system. Annealing of the ITO/PZT/Pt system and of a single ITO film was done at 400 °C in air for 1 h. The capacitances were measured using an HP 4192a impedance meter while the ferroelectric hysteresis loops were obtained by means of the Aixact TF Analyser 2000.

3. Results and discussion

The ferroelectric structure under study is shown in Fig. 1a. The top electrode ITO has been deposited on the PZT/Pt by RF sputtering. The ferroelectric and dielectric properties of this system are compared to the Pt/PZT/Pt one (see Fig. 1b) prepared under the same

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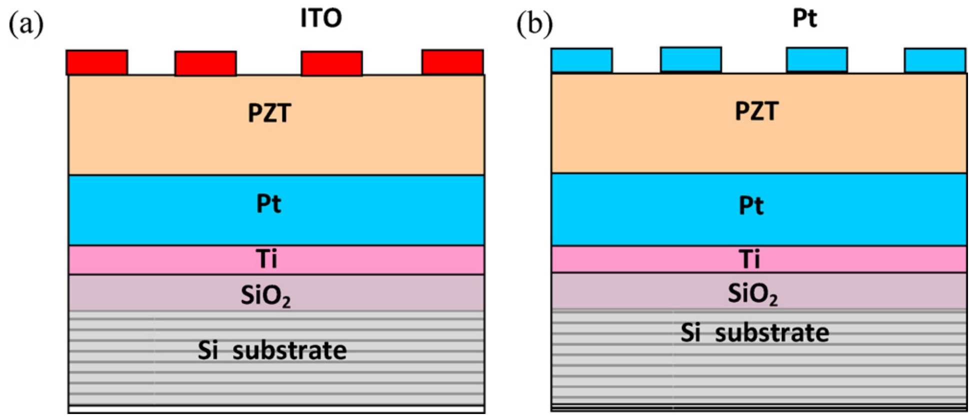

Fig. 1. The structures under study (a) ITO/PZT/Pt/Ti/SiO_2/Si and (b) Pt/PZT/Pt/Ti/SiO_2/Si.

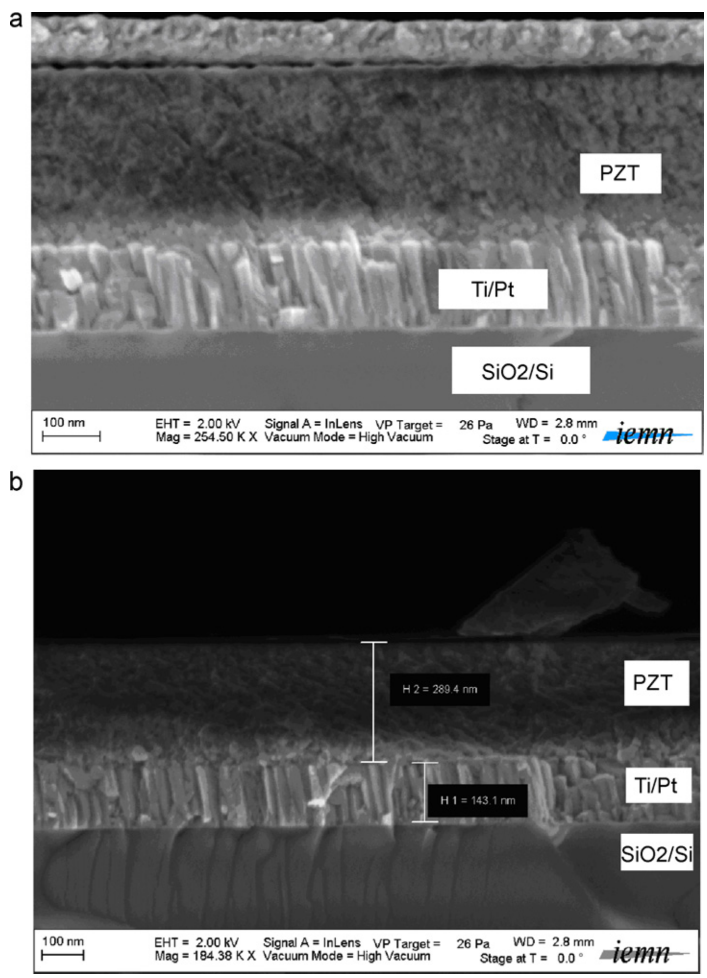

Fig. 2. SEM cross-section images for (a) ITO/PZT/Pt/Ti/SiO_2/Si and (b) PZT/Pt/Ti/SiO_2/Si.

conditions. The thicknesses for the Pt/PZT/Pt are 150 and 300 nm for Pt and PZT respectively.

In Fig. 2, we show a SEM cross-section image of the ITO/PZT/Pt/Ti/SiO_2/Si (Fig. 2a). The different layers can be distinctly seen with clear and sharp interfaces. The corresponding thicknesses are about 100 nm, 300 nm and 150 nm for the ITO, PZT and Pt respectively. Fig. 2b corresponds to a region where no ITO was deposited; the top surface is then that of the PZT layer. On this PZT surface, AFM experiments were done to study the roughness of the PZT surface on which ITO was deposited. Fig. 3 shows the two dimensional and three dimensional AFM images of the PZT/Pt/Ti/SiO_2/Si thin film. The PZT film presents homogenous and smooth surface with pyramidal shaped grains. The root-mean-square (RMS) roughness is found to be 1.650 nm.

Fig. 4 shows an XRD spectrum for the ITO/PZT/Pt/Ti/SiO_2/Si system. The peaks corresponding to ITO, PZT and Pt are identified as shown in the figure. The peaks attributed to PZT are all for the perovskite phase, confirming that the crystallization has been

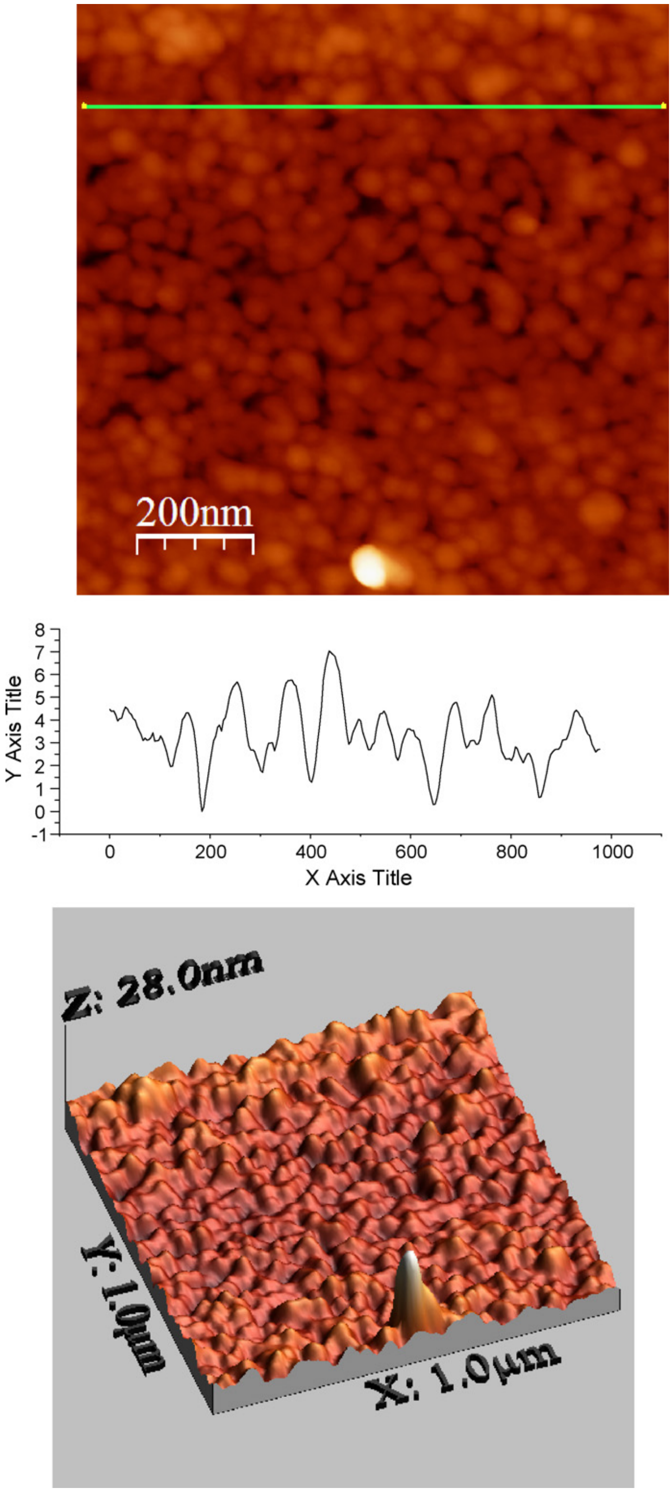

Fig. 3. Atomic force micrograph (plane and 3-D views) of PZT/Pt/Ti/SiO_2/Si.

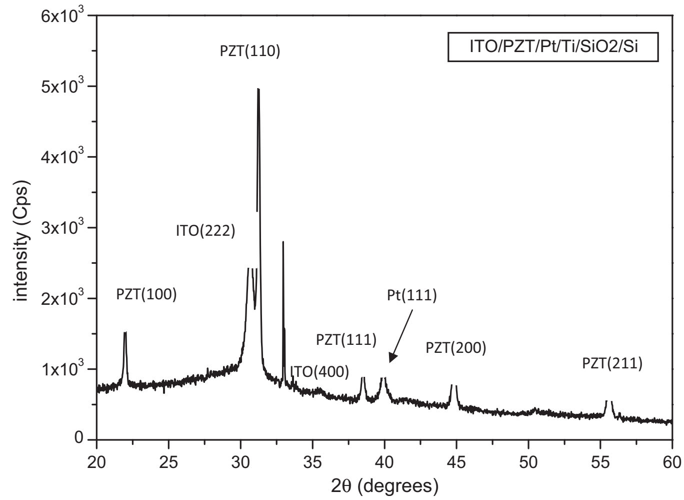

Fig. 4. XRD spectrum of ITO/PZT/Pt deposited on SiO_2/Si substrate.

achieved. X-ray diffraction experiments show thus that the films are polycrystalline with ⟨1 1 1⟩ texture for the ITO thin film, while the PZT grows with the ⟨1 0 0⟩ preferred orientation.

In Fig. 5, we show ferroelectric hysteresis loops, polarization vs electric field, for ITO/PZT/Pt and also for Pt/PZT/Pt for comparison. One can see from Fig. 5 that the two curves are practically identical. Both hysteresis loops show a symmetrical shape. It was reported that asymmetry in the hysteresis curves of such a material may arise from the pinning domains due to the presence of oxygen vacancies [11]. Thus, such a phenomenon may not exist in our sample, due to the availability of oxygen in the ITO as reported by Dunn et al. [11] in the Pt/PZT deposited on ITO.

From the hysteresis curves, we measured the maximum polarization (P_{max}), the remnant polarization (P_r) and the coercive field (E_c) for the ITO/PZT/Pt and Pt/PZT/Pt systems. These values are reported in Table 1, along with some experimental values reported in the literature for systems such as Pt/PZT/ITO (ITO as bottom electrode) [10,12,13] and ITO/PZT/ITO (ITO used as both electrodes) [14].

We note a maximum polarization P_{max} of 40 μC/cm^2 when using Pt layer as top electrode and 38 μC/cm^2 for the ITO case. The remnant polarization (P_r) is found to be about 30 and 25 μC/cm^2 for the Pt/PZT/Pt and ITO/PZT/Pt systems respectively. These values are close to the one (29 μC/cm^2) reported by Uprety et al. [5] in ITO/LNO/PZT/LNO/ITO structure and to 32.2 μC/cm^2 measured in PZT/ITO/glass, grown by a sol–gel process, by Zeng et al. [12]. These values are much higher than the one reported by Pandey et al. [13] (3.6 μC/cm^2) who explained their low P_r value by the existence of cracks in PZT/ITO/glass (deposited by sol–gel technique) due to the stress induced during phase formation and to the diffusion of Pb in the ITO films [13]. We may infer then that the relatively high value found in this work in the RF sputtered ITO/PZT/Pt sample may indicate that the sample is stress-free and no diffusion occurs at the interface ITO/PZT. Lu et al. [14] measured a higher value

Table 1
P_{max}, P_r and E_c for different structures and different preparation methods.

Structures	P_{max} (μC/cm^2)	P_r (μC/cm^2)	E_c (kV/cm)	Preparation methods	References
ITO/PZT/Pt/Ti/SiO_2/Si	38	25	90	RF sputtering	Present work
ITO/PZT/Pt/Ti/SiO_2/Si	40	30	100	RF sputtering	Present work
PZT/ITO/glass	–	32.2	–	Sol–gel	Zeng et al. [12]
PZT/ITO/glass	–	3.6	107	Sol–gel	Pandey et al. [13]
Pd/PZT/Pt/ITO/glass	52.2	15.8	100	Sputtering	Hwang et al. [10]
Pd/PZT/Pt/Ti/glass	26.7	8.1	95	Sputtering	Hwang et al. [10]
ITO/PZT/ITO	22	13	–	RF sputtering	Rao et al. [8]

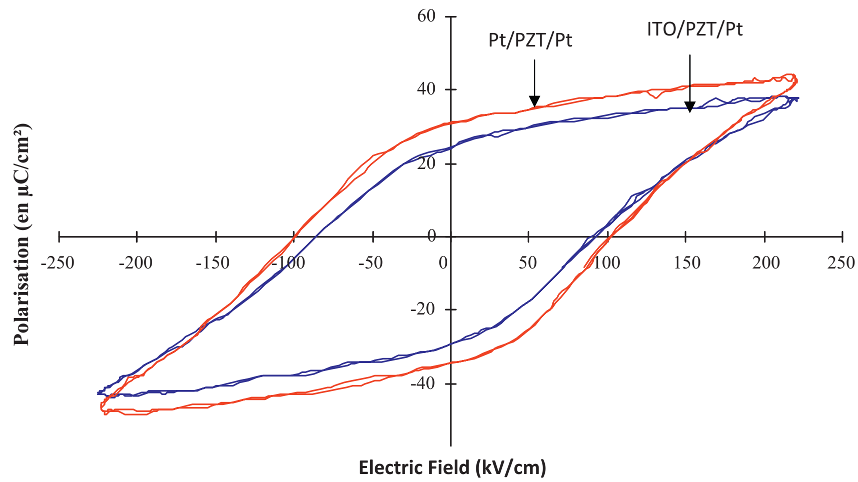

Fig. 5. Ferroelectric hysteresis loop of ITO/PZT/Pt and Pt/PZT/Pt structures.

($30\ \mu C/cm^2$) close to ours in ITO/PZT, this higher values seem to be associated to larger grain size.

As for the coercive fields, values of 100 kV/cm and 90 kV/cm were measured for Pt/PZT/Pt and ITO/PZT/Pt respectively. The values found in the present work are comparable to the one (E_c = 107 kV/cm) reported by Pandey et al. [13] in their PZT/ITO samples grown by the sol–gel technique and higher than those measured by Wang et al. [15] (around 40 kV/cm) in the PZT/LNO prepared by the modified sol–gel process. Note that in our case, E_c in ITO/PZT/Pt (90 kV/cm) is slightly smaller than E_c in Pt/PZT/Pt (100 kV/cm). In fact, a decrease in the coercive field may be associated to a better crystalline quality of the material [16] since defects tend to increase domain wall pinning effect, leading thus to an increase of E_c.

In Fig. 6, the capacitance vs the polarization field curve is shown. Such a curve is a characteristic of a ferroelectric material. Fig. 6 corresponds to a PZT film with ITO and Pt as the top electrodes as indicated in the figure. The two curves are similar mainly for the maximum value of the capacitance.

The effect of annealing of ITO/PZT/Pt film on the characteristics of the structure has been studied. In Fig. 7, we show the capacitance vs polarization curve for as-deposited and annealed ITO/PZT/Pt system (at 400 °C in air); while in Fig. 8, we present the corresponding dielectric constant ε_r. One notice that ε_r increases from 790 for the

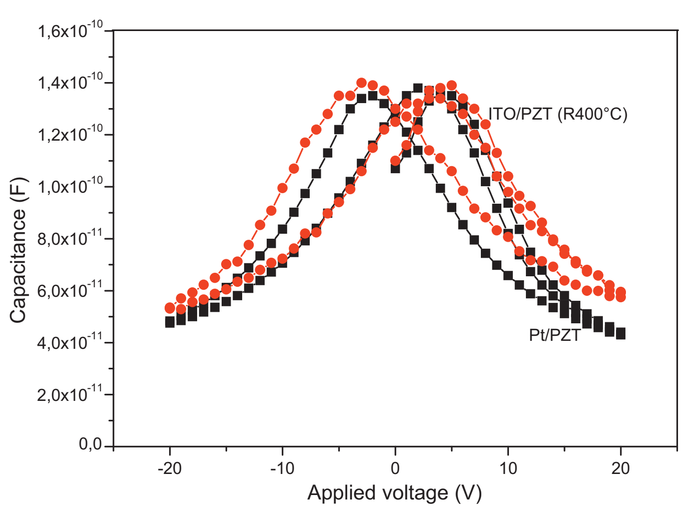

Fig. 6. Capacitance vs voltage curves for ITO/PZT/Pt and Pt/PZT/Pt.

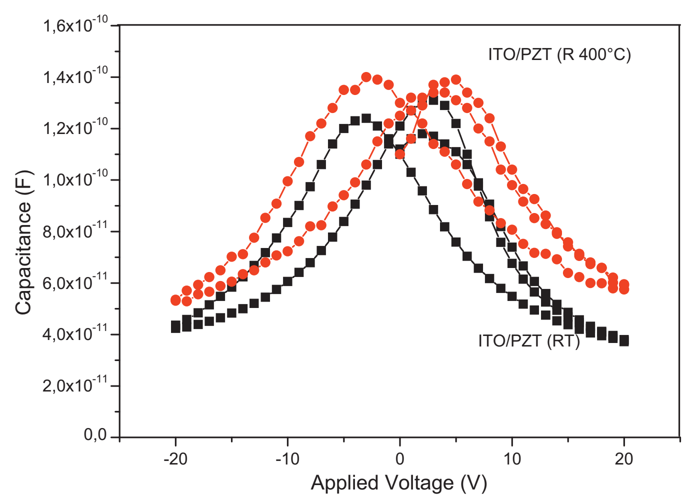

Fig. 7. Effect of annealing on the capacitance vs voltage curve for the ITO/PZT/Pt system [RT: room temperature (before annealing), 400 °C: after annealing of ITO at 400 °C in air].

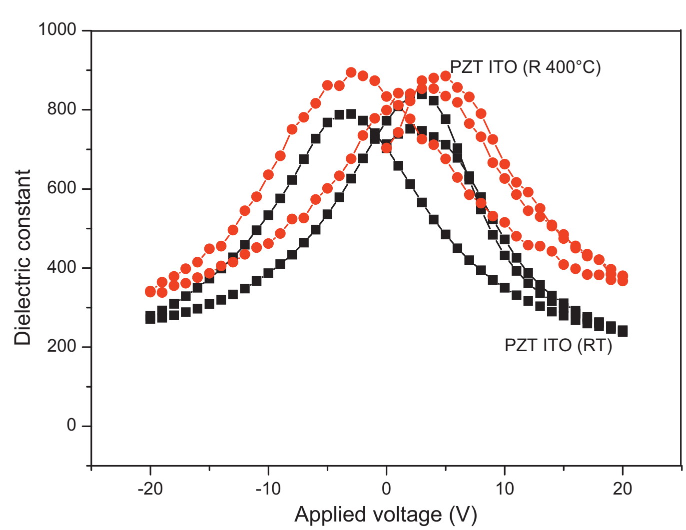

Fig. 8. Effect of annealing on the dielectric constant vs polarization voltage curve for the ITO/PZT/Pt system.

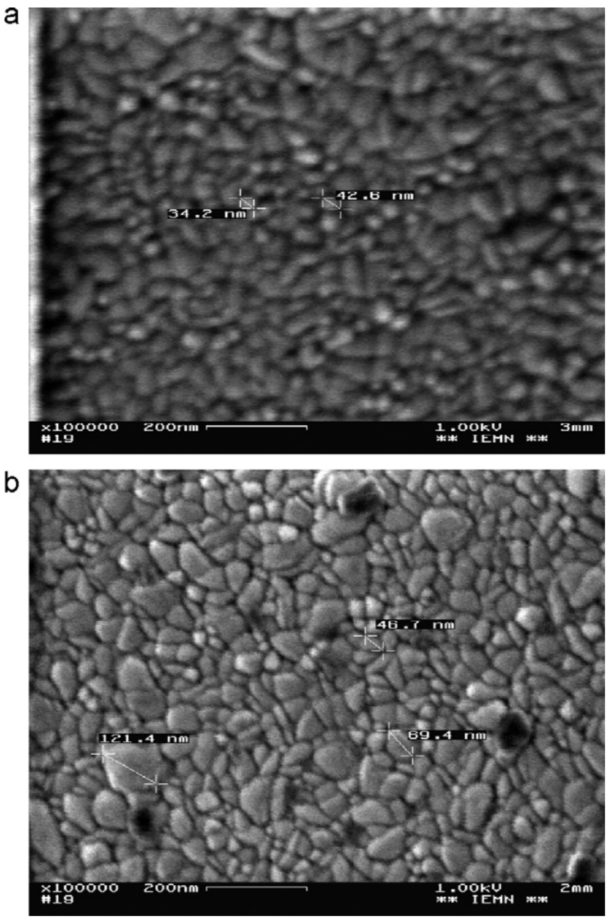

Fig. 9. SEM surface images of the ITO thin film (a) as-deposited (b) after annealing at 400 °C in air for 1 h.

as-deposited ITO/PZT/Pt to 900 after annealing which constitutes an increase of 13% in ε_r. This may be attributed to the decrease of the resistivity of ITO after annealing. Indeed, annealing may lead to a large decrease in the electrical resistivity [7].

In order to investigate the changes occurring in the ITO film after annealing, we have deposited a single thin ITO film on glass substrate at the same time as the ITO on PZT/Pt. The thickness of this single ITO film is 580 nm, the same as the thickness in the ITO/PZT/Pt structure. In Fig. 9 we show SEM images of the ITO film before (Fig. 9a) and after annealing (Fig. 9b). We clearly see an increase in the grain size. This increase in the grain size is responsible of the decrease in the electrical resistivity.

4. Conclusion

We have investigated the possibility of using ITO thin film as a top electrode in ferroelectric structure, i.e. ITO/PZT/Pt and compared the properties of this ITO/PZT/Pt system to the widely used Pt/PZT/Pt one. We have shown that RF sputtered ITO/PZT/Pt system is characterized by a smooth PZT surface and sharp interfaces; the films are polycrystalline with ⟨1 1 1⟩ texture for the ITO and ⟨1 0 0⟩ for the PZT. The ferroelectric hysteresis, the capacitance and dielectric constant curves were quite similar for both structures. We measured close values for the maximum capacitances (38 $\mu C/cm^2$ for ITO/PZT/Pt and 40 $\mu C/cm^2$ for Pt/PZT/Pt), the coercive field (90 kV/cm and 100 kV/cm) and the remnant polarization (25 and 30 $\mu C/cm^2$). Also the effect of annealing of the ITO/PZT/Pt structure on these properties has been investigated, a 13% increase of the dielectric constant was observed after annealing at 400 °C. We show then that ITO can be used as a top electrode instead of Pt and that annealing may improve further the properties of ITO/PZT/Pt.

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