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STRUCTURAL INVESTIGATIONS OF FERROELECTRIC $Pb(Zr,Ti)O_3$ THIN FILMS PREPARED BY SOL-GEL METHOD ON IrO_2 ELECTRODES

N. Popescu-Pogrion*, J. A. Johnson[a], D. Wouters[a], G. J. Norga[a], O. Van der Biest[b]

National Institute R&D of Materials Physics, Bucharest-Magurele, P. O. Box MG-07, 77125 Romania
[a]IMEC Kapeldreef 75, 3001 Leuven, Belgium
[b]K. U. Leuven, Kasteelpark Arenberg 44, B-3001 Heverlee, Belgium

The crystalline structure, the interlayer and the epitaxial growth stage of PZT/IrO_2 deposited by sol-gel method, were investigated using: X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) (in bright field (BFTEM) and in dark field (DFTEM)), in correlation with selected area electron diffraction (SAED), high resolution electron microscopy (HRTEM) and X-ray energy dispersive spectroscopy (EDS). On the IrO_2 electrodes, preferential (110) orientation was obtained. The crystalline growth of PZT film depends on the initial state of surface at the initial moment and on the relationship between PZT and bottom electrode IrO_2. In particular, the interlayer Ir_3Ti, formed between PZT and IrO_2 plays an important role in the epitaxial growth of PZT film.

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1. Introduction

Ferroelectric thin film capacitors using PZT as ferroelectric material have been investigated for memory applications. Crystallinity and growth direction of the film are very important for applications. Pt or Pt/Ti electrodes are widely used in these capacitors, because Pt has a small lattice mismatch to PZT and good heat resistance. However, PZT thin films capacitors using Pt or Pt/Ti electrodes have an important problem of fatigue. Traditionally, the ferroelectric is grown on Pt coated silicon wafers with Pt top contact electrodes.

Although with Pt the orientation and microstructure of the thin PZT films are controllable to obtain high remanent polarization values, Pt and Pt-based metal films are not the ideal bottom electrode for ferroelectric capacitors. Pt/PZT/Pt FECAPs show low endurance due to domain wall pinning at the Pt/PZT interface. In order to solve this problem, new materials [1-4] were studied. Iridium and IrO_2, are possible candidates for electrodes.

In this paper we report results on PZT thin films deposited by sol-gel method on IrO_2 electrodes. IrO_2 is a conductive oxide, with rutile structure used as a new electrode material for PZT capacitors. The relation between PZT crystallization and the IrO_2 electrode was investigated. The PZT/IrO_2 thin films did not exhibit any fatigue up to 10^{11} cycles. On the other hand, the PZT/Ir thin films start to undergo fatigue after 10^9 polarization reversals. PZT capacitors based on as-deposited IrO_2 electrodes show poor fatigue and leakage current. PZT thin films, were grown by sol-gel method and was found to have a perovskite structure [5-8].

2. Experimental procedure

$PbZr_{0.3}Ti_{0.7}O_3$ was deposited using the sol - gel method onto sputtered IrO_2 electrodes. A butoxyethanol based PZT precursor was used. Spinning conditions for deposition were 3000 rpm

* Corresponding author: pogrion@infim.ro

for 30 s followed by a 2 min hotplate drying at 200 °C and 2 min pyrolysis at 400 °C. Three layers were spun and then crystallized together for a total PZT film thickness of 130 nm. In this work, the crystallization conditions: 600 °C temperature on a hotplate for 30 min in air, were considered standard. The final sample obtained in cross- section is shown in Fig. 2

Reliable results on the microstructure of this material by means of TEM, SAED, HRTEM, EDX depend on the sample preparation. It is important to have a fresh and stable sample, free of artifacts and representative for the materials.

Two types of samples, "*plan view*" and "*cross sectional*" are usually required for the study of the microstructure of thin films. The plan view sample will give a global insight on the film microstructure while the cross-section sample can give information on the relation between film and substrates. A combination of the informations obtained from both methods will be used.

The sample prepared for *"plan view"* as small disk of 3 mm in diameter was cut from the PZT/substrates system by using an ultrasonic cutter. The disk was thereafter attached on a grinder using a special wax. The disk was manually ground to about 70-80 μm thick, dimpled and finally polished to about 15-18 μm. Ion milling was used in the final stage up to perforation.

The sample prepared for *"cross-section"* view implies the usual method of ion milling or focused-ion-beam preparation. The method has become extremely important to characterize microelectronic devices. Firstly by some slabs with a size of about 350 μm wide x 2 mm long are sliced from the received pieces. The cutting orientation is strictly determined and controlled according to the interface to be investigated.

Two pieces of clean slabs were glued together face to face by joining the film surface with the epoxy. The glued specimen stack should be heated to cure the epoxy at about 150 ^{o}C for 60 min. A grinding, dimpling and polishing procedure is applied till the specimen becomes as thin as 15-18 μm. The final ion-beam bombarding of the cross-section specimen is carried out in an ion-milling machine - Gatan Precision Ion Polishing System. The parameters used for ion milling are: 5 kV for accelerating voltage, 15 μA for the gun current and 5^{o} for the sputtering angle.

Table.1 Characterizations of the PZT samples.

Sample	Final annealing conditions	Thickness of the IrO_2 layer	Grain size (μm)	Mean size of the grains (μm)
D05	600 ^{o}C, 30 min. Hot plate	50 nm	2.0 – 4.88	2.837
D12	600 ^{o}C, 30 min. (O_2)	100 nm	1.58 – 4.02	1.925

3. Results

Statistical determinations (the distribution of the grain size and the mean size diameter), which reveal the uniformity and quality of PZT layers have been carried out on the basis of four specimens obtained from each sample. Around 500 grains for each sample (D5 and/or D12) have been counted (see Fig. 1).

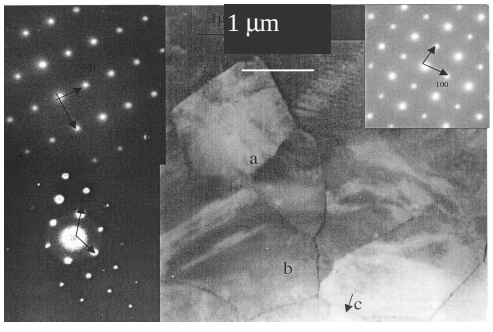

Fig. 1. Plan view of D5.

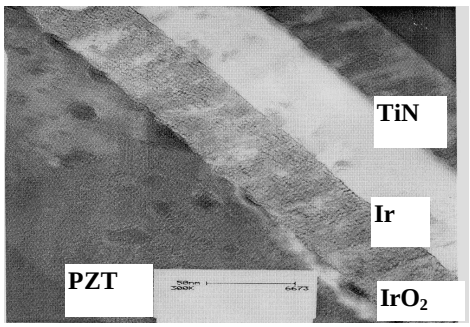

Fig. 2. Cross sectional view of D12.

The measurements of the grain size have been carried out using transmission electron microscopy images (plan view). The distribution of the grain size and the variation of the mean value of diameter has been calculated. The mean diameter for both samples was in the range 1.58 - 4.88 μm.

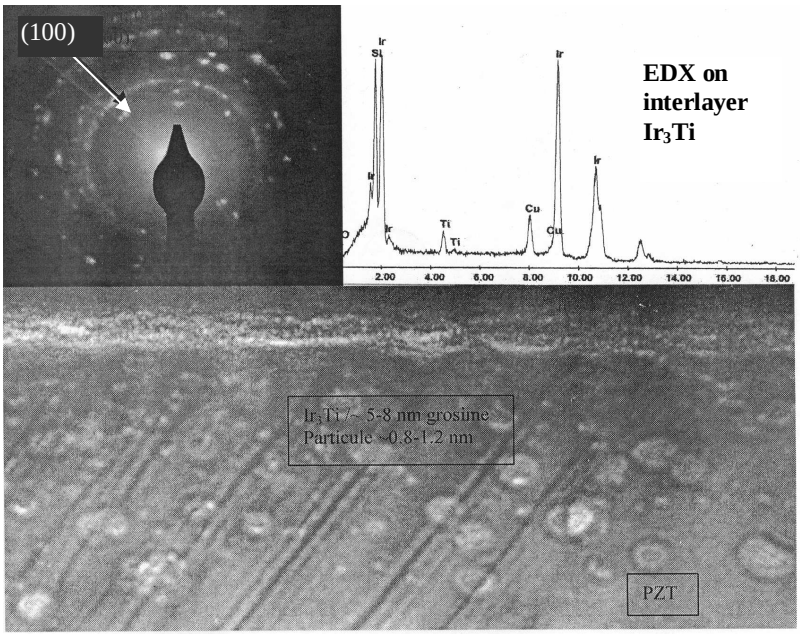

Fig. 3. SAED, EDX and TEM on interlayer Ir_3Ti.

Fig. 1 shows the plain view of the sample D5. The sample exhibits a homogeneous microstructure without pores and defects (such as dislocations and stacking faults). The electron diffraction patterns have revealed [100] -grain "a", [110] -grain "c" and [111] - grain "b", pseudocubic zone axes.

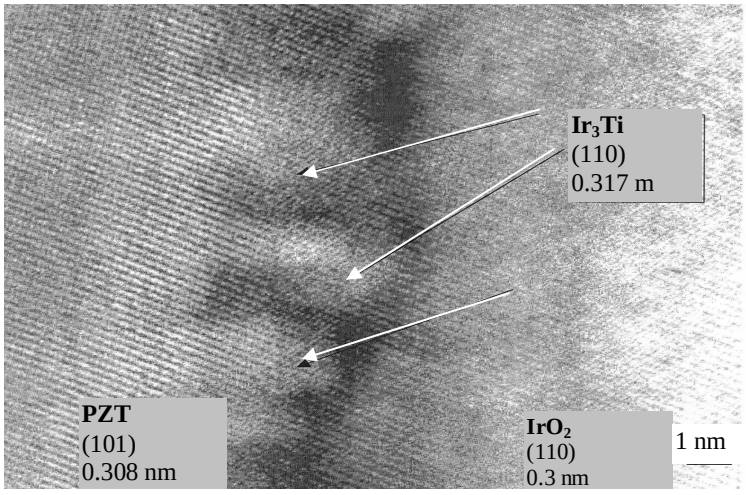

Fig. 4. High resolution transmission electron microscopy on PZT/IrO_2.

Fig. 3 shows the interface between PZT/IrO_2. A special analysis has been performed in this interlayer by transmission electron microscopy, selected area electron diffraction and X-ray energy dispersive spectroscopy.

Transmission electron microscopy investigations (TEM) in correlation with energy dispersive X-ray analysis (EDX) and selected area electron diffraction (SAED) of the interfacial layers revealed that, between the PZT and the IrO_2, grows an Ir_3Ti layer (Fig. 3), characterized by cubic Pm3m (221) $AuCu_3$ type structure with calculated a = 0.37882 nm practically identical with the value a = 0.3843 nm published in ASTM Powder Diffraction File. The interfacial layer, thick up to 8 nm is formed by nanoparticles with the size 0.55 -1.08 nm.

The complex structural investigations (TEM+SAED+EDX) (Fig. 3) and (HRTEM) (Fig. 4) of the interface have revealed: an epitaxial layer PZT/IrO_2 (35% along of the grain boundaries in presence of Ir_3Ti) and grain boundaries without Ir_3Ti - 65%.

4. Summary

There were determined the morphology of the PZT grains and the orientation of grains as a function of size. TEM (SAED)/ HRTEM) /EDS investigations revealed the presence of a polycrystalline Ir_3Ti layer at the interface PZT /IrO_2. This paper evidences the epitaxial growth along (101) or (110) PZT planes on the (110) IrO_2 substrate.

The <110>, <100> and <111> growth directions were studied and discussed.

This paper reports: the grains morphology of the sol-gel PZT films, the size of the grains, the dependence between the orientations and the size of the grains, the uniformity of the layers the morphology of the grain boundaries in plan view and in cross-sectional view, the morphology and the identification of the interlayer between PZT and IrO_2.

The grain size has a dominant effect in the formation of defects and orientation of the grains. The interlayer between PZT and IrO_2 has a thickness in the range 5 - 8 nm and is formed by nanocrystals with the size around 0.55 nm.

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