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Bottom electrode crystallization of PZT thin films for ferroelectric capacitors

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Abstract

The bottom electrode crystallization (BEC) method was applied to the crystallization of PZT thin films deposited by laser ablation over $Si/SiO_2/Ti(Zr)/Pt$ structures, with the platinum films being deposited at two different temperatures. The results were compared with those obtained by rapid annealing with halogen lamps and furnace annealing. PZT films crystallized over Pt made at lower temperature with Ti adhesion layers tend to have a (1 1 1) preferential orientation, while those deposited on platinum made at higher temperature tend to have a (1 0 0)/(1 1 1) mixed orientation. When Zr adhesion layers are used, the PZT films crystallized over Pt have a preferential (1 0 0) orientation, except for films deposited over Pt made at 500 °C and crystallized with a high heating rate. The ferroelectric properties of the films crystallized with the BEC method are good, being similar to those obtained with the other crystallization methods using the same parameters.

Keywords: Films; Electron microscopy; Ferroelectric properties; PZT; Capacitors

1. Introduction

The preferred orientations as well as the ferroelectric and piezoelectric properties of PZT thin films are intensively studied as a function of the deposition conditions and annealing temperatures.[1,2] In particular, the method used for the crystallization of PZT thin films plays a key role in the final achieved properties, influencing the preferred orientation, the grain size and the amount of lead lost during crystallization of the films.[3,4]. Regarding the heating rates, the crystallization methods can be classified as slow (classic furnace annealing) with rates up to 1 °C/s or fast (rapid thermal annealing) with higher heating rates. The rapid thermal annealing (RTA) techniques are widely used for crystallization of thin films. Previous investigations showed that the use of RTA in the area of ferroelectric thin films took advantage of the short time processing, reducing the time-temperature product so that the pyrochlore phase was suppressed while enhancing the perovskite phase formation.[5–7]

Rapid annealing using halogen lamps and Joule heating was recently used for crystallization of amorphous silicon and for the fabrication of polycrystalline silicon devices.[8,9] A new method for crystallization of thin films deposited on $Si/SiO_2/Ti/Pt$ using the Joule effect in the bottom electrode has recently been reported.[10] The bottom electrode crystallization (BEC) method proved to be inexpensive and versatile, providing precise temperature control. The use of BEC can easily and accurately reproduce the slow and fast heating rates used in furnace and rapid thermal annealings (RTA), respectively.

The adhesion layers used at the interface between SiO_2 and Pt and the platinum deposition conditions also play a key role in the final properties of the capacitors due to the diffusion processes and/or changes in the stress state of the platinum electrodes.[11–14] As previously reported, different metals like Ti, Zr, Ta, Ru and their oxides have been used as buffer layers. Maeder et al. demonstrated that zirconium has a very good adhesion to both silica and platinum and excellent barrier layer properties for both lead and silicon diffusion but no ferroelectric properties of PZT thin films were investigated using Zr adhesion layers.[11]

In the present work we study the properties of PZT thin films deposited by laser ablation on $Si/SiO_2/Ti/Pt$ or $Si/SiO_2/Zr/Pt$ substrates and crystallized using the BEC method. As a comparison, the properties of PZT films deposited under

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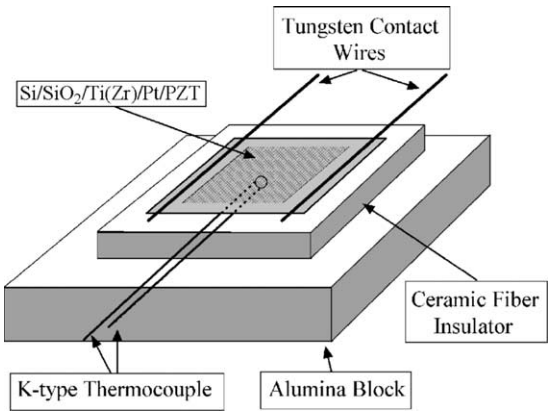

Fig. 1. Experimental setup for the BEC method.

the same conditions and crystallized with the same heating and cooling rates using the furnace annealing and rapid thermal annealing methods were also investigated.

2. Experimental

Silicon wafers with (1 0 0) orientation were cut for obtaining 1 cm × 1.5 cm substrates. After oxidation at 950 °C in wet oxygen for 72 h, a SiO_2 layer of approximately 1 μm was obtained. The Pt, Ti and Zr layers were deposited using the RF magnetron sputtering technique in Ar with 2 in. diameter targets, using a sputtering chamber having a base pressure of 10^{-6} mbar. Titanium and zirconium layers with thicknesses of 30 nm were sputtered at 200 °C using an RF power of 150 W and a deposition pressure of 1×10^{-2} mbar. Platinum films, 200 nm thick, were deposited on the adhesion layers (Zr or Ti) at temperatures of 200 or 500 °C using the same values for the RF power and deposition pressure.

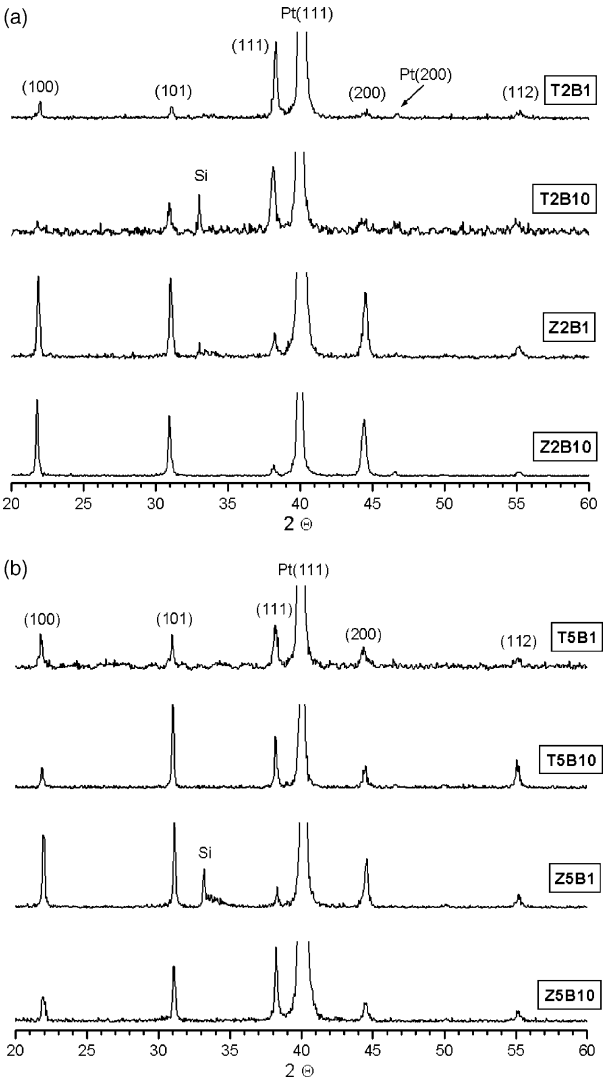

Fig. 2. X-ray diffraction patterns of PZT films crystallized using the BEC method over platinum films deposited at (a) 200 °C, and (b) 500 °C with Zr and Ti adhesion layers.

Table 1
Preparation conditions for the electrodes

Sample name	Buffer layer	Platinum deposition temperature (°C)	Heating and cooling rates (°C/s)	Crystallization time (min)	Heat treatment method
T2B10	Ti	200	10	1	BEC
T2H10					Halogen lamps
T2B1			1	10	BEC
T2F1					Furnace
T5B10	Ti	500	10	1	BEC
T5H10					Halogen lamps
T5B1			1	10	BEC
T5F1					Furnace
Z2B10	Zr	200	10	1	BEC
Z2H10					Halogen lamps
Z2B1			1	10	BEC
Z2F1					Furnace
Z5B10	Zr	500	10	1	BEC
Z5H10					Halogen lamps
Z5B1			1	10	BEC
Z5F1					Furnace

$Pb(Zr_{0.52},Ti_{0.48})O_3$ films were deposited by laser ablation using 1.5 cm diameter targets. For obtaining the PZT targets, lead carbonate, zirconium and titanium oxides were mixed in stoichiometric proportions with 10% excess lead and calcined at 900 °C for 1 h, to form the pure perovskite phase. Fine PZT powder (<5 μm) was obtained after milling for several hours in a planetary mill. Circular pellets were prepared by uniaxially pressing at 200 MPa. In order to obtain dense PZT ceramics, the PZT samples were sintered at 1250 °C for 2 h, with an O_2 flux and in the presence of lead zirconate packing powder.

The PZT films approximately 500 nm thick were deposited at room temperature using a KrF laser (λ = 248 nm) with a fluence of 3.5 J/cm^2 and a repetition rate of 15 Hz for a deposition time of 45 min. The depositions were carried out in 2×10^{-2} mbar O_2 atmosphere with a target-substrate distance of 4 cm. The thickness of the PZT films was kept constant for all the samples analyzed in this study. The films were crystallized using furnace annealing, rapid thermal annealing or bottom electrode crystallization method. The furnace annealing was carried out in oxygen flow with a heating and cooling rate of 1 °C/s, a maximum temperature of 650 °C and a crystallization time of 10 min. The rapid thermal annealing was applied using two halogen lamps of 500 W each. The heating and cooling rates were 10 °C/s, the maximum temperature was also 650 °C and the crystallization time was 1 min. The bottom electrode crystallization method was applied with the same parameters used for furnace annealing and rapid thermal annealing, respectively. Table 1 summarizes the conditions used for the crystallization of the films.

The BEC method was applied using the setup shown in Fig. 1. A current source (maximum current of 3 A) was used to apply a current to the platinum films by means of electrical contacts made on two opposite edges of the bottom electrodes using tungsten wires 0.5 mm thick; the distance between the contacts was 10 mm. A multimeter was used for reading the temperature from a thermocouple under the sample. The samples were placed over a high temperature ceramic fiber insulator. A LabWiev program was used for handling the heat treatments through a simple proportional control algorithm.[10]

After the crystallization of the PZT films, aluminum top electrodes with a surface of 0.1 mm^2 were deposited by thermal evaporation using shadow masks. The ferroelectric properties of the films were investigated by analyzing the hysteresis loops using a Sawyer-Tower circuit with a frequency of 100 Hz. The ferroelectric fatigue of the films was evaluated up to 10^{10} switching cycles using pulses of 250 kV/cm for aging and a maximum field of 300 kV/cm for measurement. The aging field value was chosen in order to avoid dielectric breakdown before 10^{10} cycles. Up to 10^5 cycles, the frequency used for measurements was 100 Hz, after that changing to 50 kHz. The crystalline phases and orientations were identified by X-ray diffraction and the microstructure of the films was studied by scanning electron microscopy (SEM).

3. Results and discussion

The X-ray diffraction analyses of the PZT films crystallized using BEC method are shown in Fig. 2. All the PZT

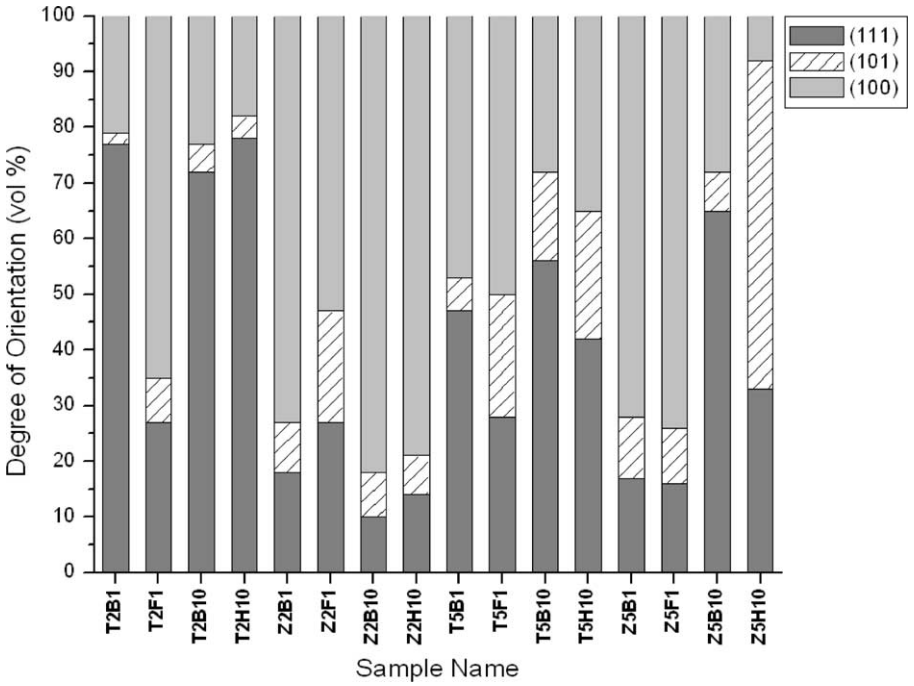

Fig. 3. PZT orientation as a function of the adhesion layers, Pt deposition temperatures and crystallization methods.

peaks can be assigned to the perovskite phase, with no traces of pyrochlore being detected in the diffractograms. In the part (a) of Fig. 2 are plotted the results obtained after the crystallization of the PZT on platinum deposited at 200 °C. One can see that PZT films deposited over Ti/Pt tend to orient in the (1 1 1) direction independent of the heating and cooling rates used, while the films deposited over Zr/Pt tend to orient in the (1 0 0) direction. The part (b) of Fig. 2 shows the crystallographic orientation of the PZT films crystallized over platinum deposited at 500 °C. In this case the films deposited over Ti/Pt show a mixed (1 0 0)/(1 1 1) orientation while when deposited over Zr/Pt, the main orientation was (1 0 0) for low heating rates and (1 1 1) high heating rates.

Fig. 3 shows the main orientations of the PZT films crystallized with different methods and conditions. The degree of orientation D_n for each crystalline direction (n) was calculated using the expression:

$$D_n = \frac{I_n(I^{C}_{(1\,0\,1)}/I^{C}_{n})}{\sum_n I_n(I^{C}_{(1\,0\,1)}/I^{C}_{n})} \times 100 \quad (1)$$

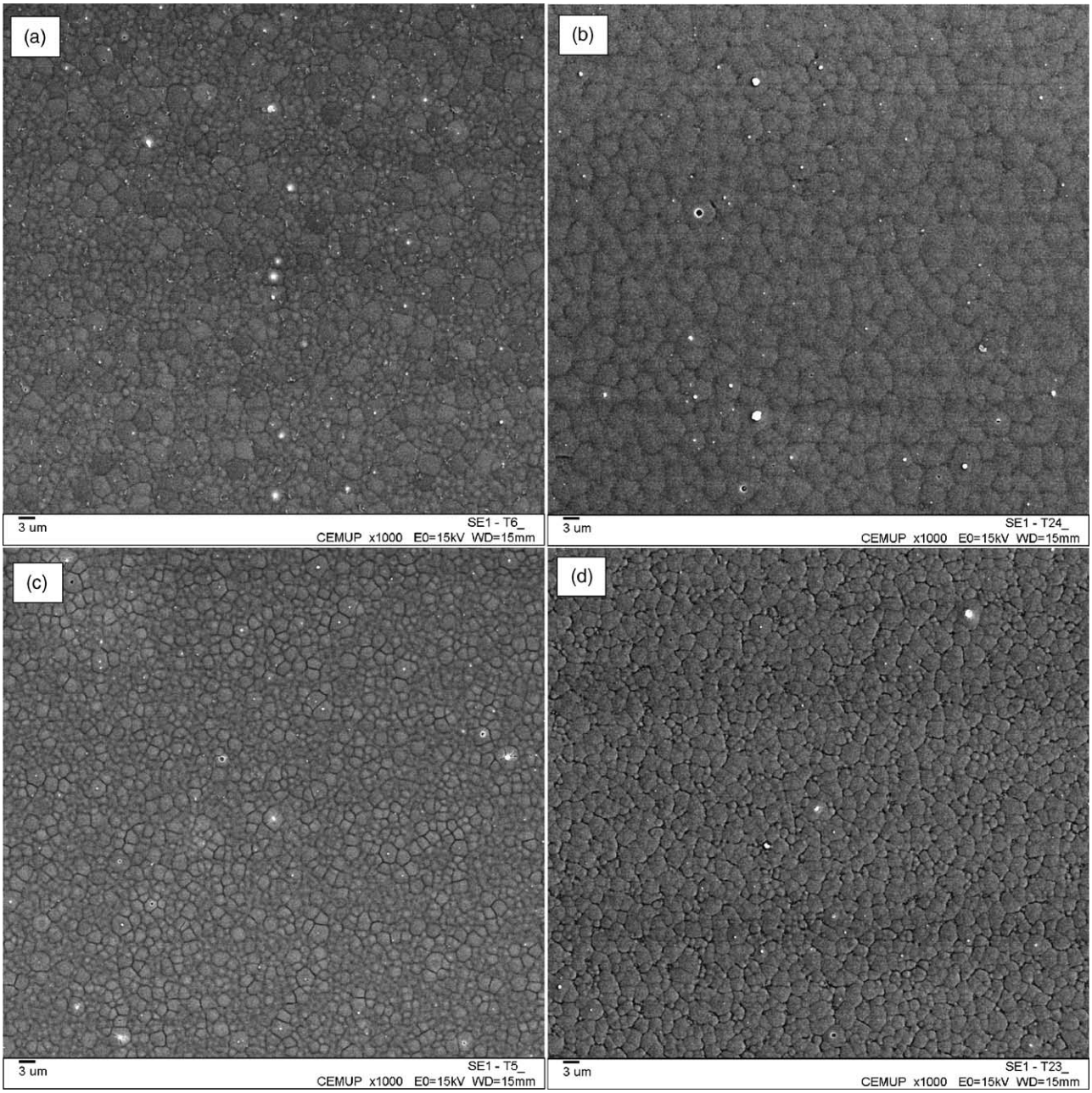

Fig. 4. Scanning electron micrographs of the surfaces of PZT films deposited over Ti/Pt films made at 500 °C and crystallized using: (a) RTA 10 °C/s; and (c) BEC 10 °C/s and PZT films deposited over Zr/Pt films made at 200 °C and crystallized using: (b) furnace annealing 1 °C/s; and (d) BEC 1 °C/s.

where I_n is the intensity of each peak measured from the X-ray pattern, I_n^C is the relative intensity of each peak from the powder diffraction file card for $Pb(Zr_{0.52},Ti_{0.48})O_3$ and $I_{(1\,0\,1)}^C$ is the intensity of the main (1 0 1) peak from the card.

Comparing the results obtained from BEC with the ones obtained from halogen RTA and furnace crystallization, one can see that the PZT orientations are very similar, except in the cases of PZT deposited over Ti/Pt made at 200 °C and crystallized with a low heating rate and of PZT deposited over Zr/Pt made at 500 °C and crystallized with a high heating rate. One can also notice that the percentage of (1 0 1) orientation tends to be smaller for films crystallized with BEC.

The changes in the PZT orientations as a function of the crystallization method, the buffer layer used and the Pt deposition temperature are influenced by a complex combination of factors. As previously reported, Pt films made at low temperatures are under compressive stress,[12,15] whereas the ones deposited at high temperature are under tensile stress after cooling due to the larger thermal expansion coefficient for Pt compared to the one for the substrate (8.8×10^{-6} and $2.6 \times 10^{-6}\,K^{-1}$ at room temperature, respectively).[16] For the deposition conditions used in this study, Pt films made at 200 °C should be under compressive or low tensile stress whereas the ones deposited at 500 °C are under tensile stress. This behavior is independent of the type of adhesion layer due to the big difference in thickness between the Pt and Ti/Zr films (200 and 30 nm, respectively). Hence the difference in the orientation of the PZT films should be related with the different diffusion behaviors of Ti/Zr in the Pt, Pb diffusion from the PZT and the related stress changes which occur in Pt and PZT during the crystallization process. Due to the fact that Zr does not diffuse in the Pt, the Pt stress is different from the case when the Ti buffer layer is used.[11]

In Fig. 4 are presented the scanning electron micrographs of PZT films deposited over platinum made at 500 °C with Ti adhesion layers and crystallized with high heating rates and of PZT films deposited over platinum made at 200 °C with Zr adhesion layers and crystallized with low heating rates. Comparing the surfaces of the PZT films crystallized with high heating and cooling rates using halogen RTA (Fig. 4a) and BEC method (Fig. 4c), one can see that the films present similar features regarding the grain sizes (between 2 and 5 μm) and surface smoothness. In the case of using slow heating and cooling rates for the crystallization of PZT, the film crystallized in the furnace (Fig. 4b) shows slightly bigger grain sizes than the film crystallized by BEC (Fig. 4d). All the PZT films presented a dense and uniform microstructure.

The ferroelectric properties of the PZT films crystallized using the BEC method were compared with those from the films crystallized using the other two methods. The PZT films crystallized by different methods over Pt/Ti layers presented comparable results for the same heating rates and platinum deposition temperatures, as expected from the results obtained with SEM. In Fig. 5 are shown the ferroelectric hysteresis loops for PZT films deposited over platinum made at 200 or 500 °C and crystallized with high heating rates using halogen RTA and BEC method. The ferroelectric properties of the PZT crystallized over Pt made at 500 °C show higher values for remanent polarization (around 32 μC/cm^2)

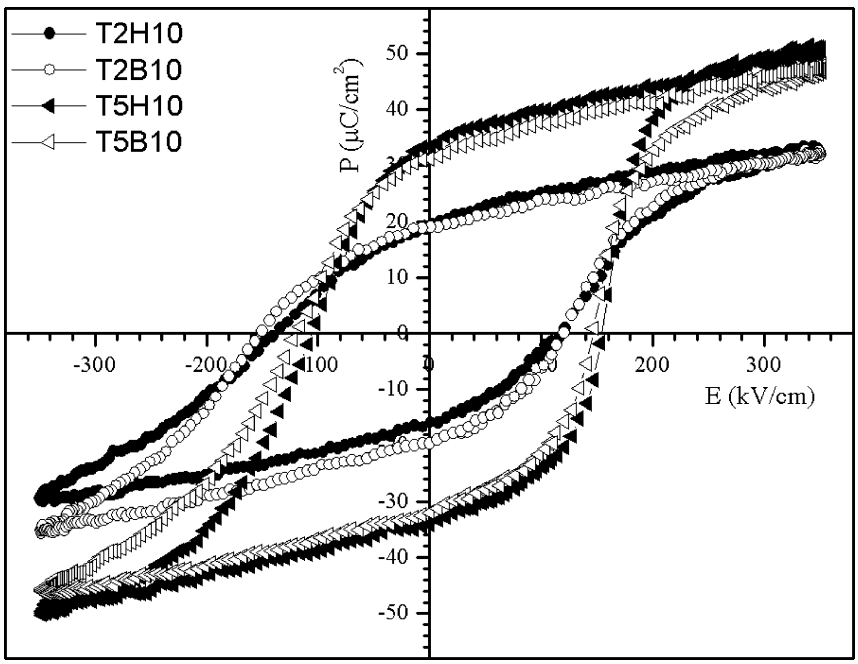

Fig. 5. Ferroelectric hysteresis loops for PZT films crystallized over platinum made at 200 and 500 °C using halogen RTA and BEC methods with Ti adhesion layers.

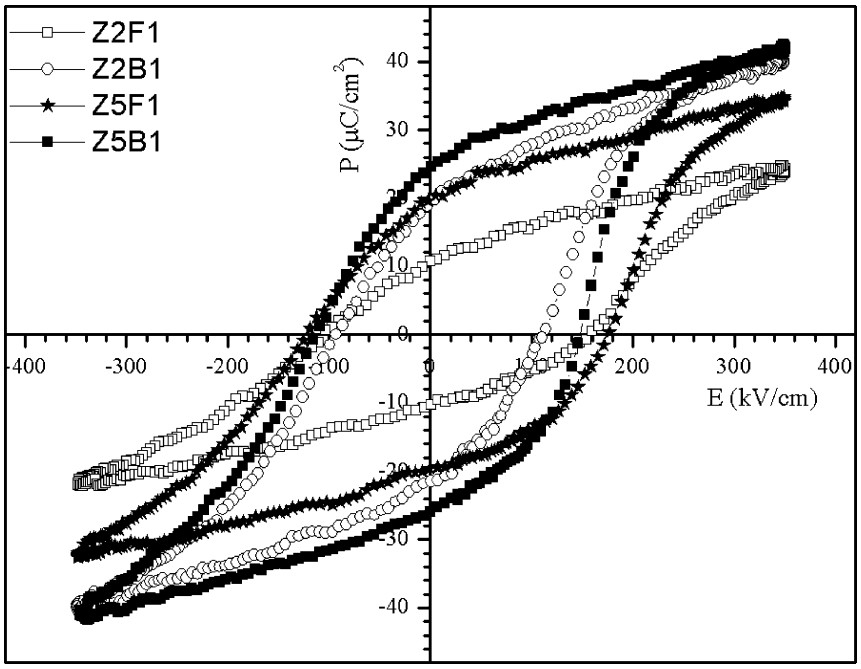

Fig. 6. Ferroelectric hysteresis loops for PZT films crystallized over platinum made at 200 and 500 °C using furnace annealing and BEC methods with Zr adhesion layers.

than those deposited over Pt made at 200 °C. The values for the coercive field are similar for all the four samples.

For the case of PZT films deposited over Pt made at 200 or 500 °C with Zr adhesion layers, in Fig. 6 one can see that the ferroelectric hysteresis loops for films crystallized with low heating rates by BEC and furnace annealing does not present similar results anymore. For both platinum deposition temperatures the loops corresponding to the BEC method presented higher values for remanent polarization and smaller values of the coercive field when compared with the ones corresponding to the furnace annealing.

Fig. 7 shows the results obtained from fatigue measurements performed on PZT films deposited over platinum made at 200 °C with Ti and Zr buffer layers and heat treated

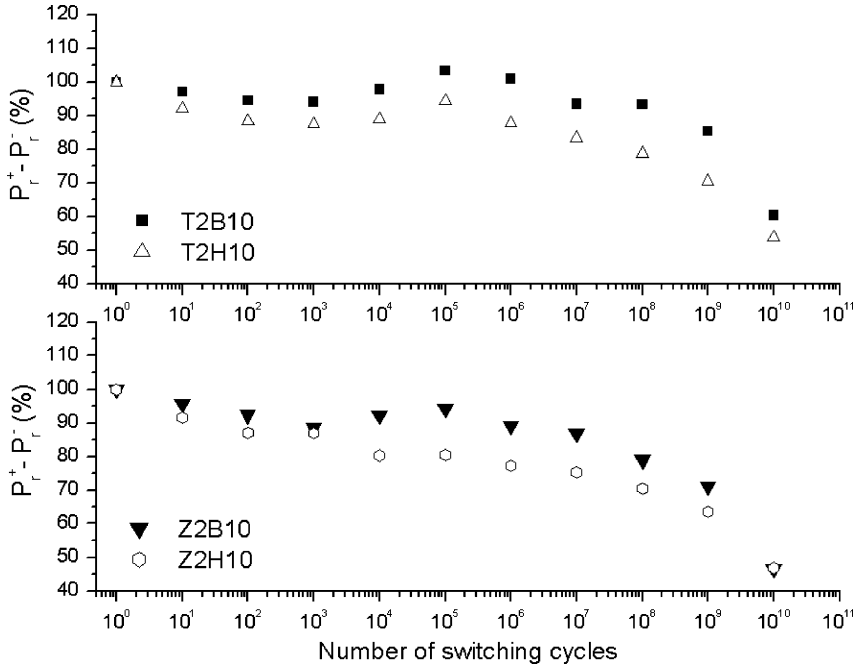

Fig. 7. Ferroelectric fatigue for PZT films deposited over Pt made at 200 °C with Zr and Ti adhesion layers and crystallized using BEC and halogen RTA methods.

with high heating rates using different methods. After 10^{10} switching cycles the remanent polarizations decreased to approximately 60% of the initial values, when the adhesion layer used was Ti, and to approximately 50% of the initial values when Zr was used. The results are similar or slightly better when using the BEC method for crystallization.

4. Conclusion

PZT thin films deposited by laser ablation over $Si/SiO_2/Ti(Zr)/Pt$ structures were crystallized using different methods. The effect of platinum deposition temperature and heating rates for crystallization was also studied. The results obtained using the bottom electrode crystallization (BEC) method were compared with those obtained by rapid annealing with halogen lamps and furnace annealing. PZT films crystallized over platinum made at lower temperature with Ti adhesion layers tend to have a (1 1 1) preferential orientation, while those deposited on platinum made at higher temperature tend to have a (1 0 0)/(1 1 1) mixed orientation. When Zr adhesion layers are used, the PZT films crystallized over Pt have a (1 0 0) preferential orientation, except for the films deposited over Pt made at 500 °C and crystallized with a high heating rate. The PZT films crystallized by BEC tend to have a smaller percentage of (1 0 1) orientation when compared to the films crystallized by other methods. The ferroelectric properties of the PZT films crystallized with the BEC method are good, being similar or better than those obtained with the other crystallization methods using the same parameters.

The BEC method is a very simple, inexpensive and efficient method for crystallization of thin films, having power consumption under 20 W for the heat treatments used in this study. A wide range of temperatures and heating rates can be used and the low thermal inertia allows a precise temperature control.

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