Optimization of the Fabrication Parameters of PZT 52/48 Thin Films by Pulsed Laser Ablation

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Abstract. Thin films of $PbZr_{0,52}Ti_{0,48}O_3$ (PZT) for applications in piezoelectric actuators were deposited by the pulsed laser deposition technique (PLD) over $Pt/Ti/SiO_2/Si$ substrates. The effect of different electrode and PZT deposition and processing conditions on the ferroelectric and piezoelectric properties of the devices was investigated. X-Ray diffraction results showed that the deposition temperature for the electrodes had a strong influence on the PZT orientation; the increase in the electrode deposition temperature changes the PZT orientation from random or (111) to (001) depending also on PZT deposition pressure. From scanning electron microscope (SEM) pictures one could also observe that the deposition pressure affects the porosity of the PZT films, which increases with the pressure above 1×10^{-1} mbar for films deposited at room temperature. The measurement of the ferroelectric hysteresis curves confirmed that the structural changes induced by different processing parameters affected the ferroelectric properties of the material. The best ferroelectric properties including fatigue endurance were obtained for electrodes made at high temperature and for PZT deposited at 2×10^{-2} mbar and heat treated at 675ºC for 30 minutes in an oxygen atmosphere. The piezoelectric coefficient d_{33}, measured using a Michelson interferometer, had values in the range between 20 and 60 pm/V, and showed a strong dependence on the thickness of the PZT films.

Introduction

The $PbZr_xTi_{1-x}O_3$ (PZT) ceramics exhibit superior ferroelectric, piezoelectric, and pyroelectric properties. Therefore these materials are used in a wide range of applications such as actuators, force sensors, optical infrared sensors, and ferroelectric memories. In order to use these ceramics to their full potential, thorough research of their properties is needed [1].

Bulk ferroelectric ceramic actuators have certain shortcomings such as low fracture toughness, high inertia, and relatively large size. As a result, the range of working frequencies is limited, the dimensions are large in relation to the structure under investigation and adhesion of the piezoceramic to a structure is difficult due to different curvatures and surface roughness. Ferroelectric ceramic in thin film form have several key advantages over bulk materials as active elements in electromechanical devices. Thin films require a low driving voltage and have small inertia, which allows for higher frequency operation of the devices. Ferroelectric thin film investigations are manly focused on film thickness of less than 10 μm for application on silicon structures with features from a few μm to 10 μm [1].

The properties of ferroelectric thin films are critical to quality and reliability of micro-electromechanical devices [2]. Due to their planar geometry, high residual stress state and degree of orientation, ferroelectric thin films are expected to behave differently from bulk ferroelectric ceramics. In order to optimize the film properties and performance it is essential to understand the

factors that influence these properties and, in recent, an extensive experimental work was carried out on the characterization of these ferroelectric thin films [3].
The main objective of this work is to study the properties of Si/SiO2/Ti/Pt/PZT/Al stacks in order to optimize its piezoelectric properties so it can be used as micro-actuator for integrated optic devices.

Sample Preparation

Silicon (100) substrates, 1×2 cm^2 were oxidized in an oxygen flow for 72 hours at 950ºC in order to create a SiO_2 layer of 1 μm thickness. Two metallic layers were deposited on those substrates by RF Magnetron Sputtering: titanium with 20 nm of thickness and platinum with 200 nm. The Ti layer works as a buffer layer and as an adhesion enhancer for the Pt thin film. The Pt is the bottom electrode for the piezoelectric thin film. In table 1 the deposition conditions for the Ti and Pt thin films are given. All films were deposited in argon atmosphere, with a pressure of 1×10^{-2} mbar using 150 W RF power onto 2" diameter targets placed 8 cm from the substrates. Film thicknesses were measured during deposition, with a quartz crystal based thickness monitor.

Sample Set	Material	Deposition Temperature (ºC)
01	Ti	25
	Pt	25
05	Ti	25
	Pt	500
11	Ti	200
	Pt	500

Table 1: Deposition conditions for the metallic thin films deposited by RF Magnetron Sputtering.

The PZT thin films were deposited by laser ablation using a pulsed KrF laser (Lambda Physics 305i) and an ultra-high vacuum chamber system with a load lock chamber and a base pressure of at least 2×10^{-7} mbar. The fluence used for all depositions was 2 J/cm^2, the laser frequency was 20 Hz and the distance between the target and the substrate was fixed at 4 cm. The targets were made by cold pressing PZT nanometric particles followed by sintering at 1250ºC for 1 hour; they had a Zr/Ti ratio of 52/48, with a 10% weight excess of PbO and a density of 96%. They were rotated at 10 rpm during deposition; its surface was polished with sandpaper before each process. The depositions were made at room temperature (25ºC) and this implied a post-deposition heat treatment in order to promote the growth of the PZT perovskite phase. The heat treatments were carried out in a tubular furnace with an oxygen atmosphere; the samples were introduced in the furnace tube already set at the desired temperature (between 600 and 675ºC). After heat treatment Al top electrodes were deposited by thermal evaporation using shadow masks.
The thin film orientation was determined by x-ray diffraction (XRD), the thickness was measured by a DEKTAK IIA stylus profilometer and the sample surface was analyzed with the scanning electron microscope (SEM) technique. The effective piezoelectric small-signal coefficient (d_{33}) and large-signal strain (S) was measured using a Michelson laser interferometer with a heterodyne scheme for the signal measurement and an Argon Ion laser; the measurements were made applying a sinusoidal signal of 2.5 kHz with a DC offset [4]. The ferroelectric properties were measured using a modified Sawyer-Tower circuit using a sinusoidal test signal at 100 Hz with automatic computer control based on the IEEE488 [5].

Results and Discussion

Figure 1(a) depicts the XRD measurements made on PZT thin films deposited on substrates with electrodes made using the deposition conditions from SET02. In this case the time was kept constant at 20 minutes varying the O_2 pressure in the range from 2×10^{-4} to 1 mbar. The results show that at the highest pressure (1 mbar) the films exhibit a strong (101) orientation while at lower pressures the films are (111) oriented. Another important effect of the deposition pressure can be observed in the microstructural characteristics of the films: the ones made at 1 mbar are not fully compact being easily removed from the substrates, while those deposited at 2×10^{-4} mbar exhibited a large number of fractures due to the high level of residual mechanical stress. For these reasons, the 2×10^{-2} mbar pressure was considered to be the best one, taking into account the remaining deposition parameters. For improving the ferroelectric properties of those films, the 675ºC/30 minutes heat treatment in an oxygen atmosphere was the optimal one. Figure 1(b) shows a ferroelectric hysteresis loop for a PZT thin film made with these conditions.

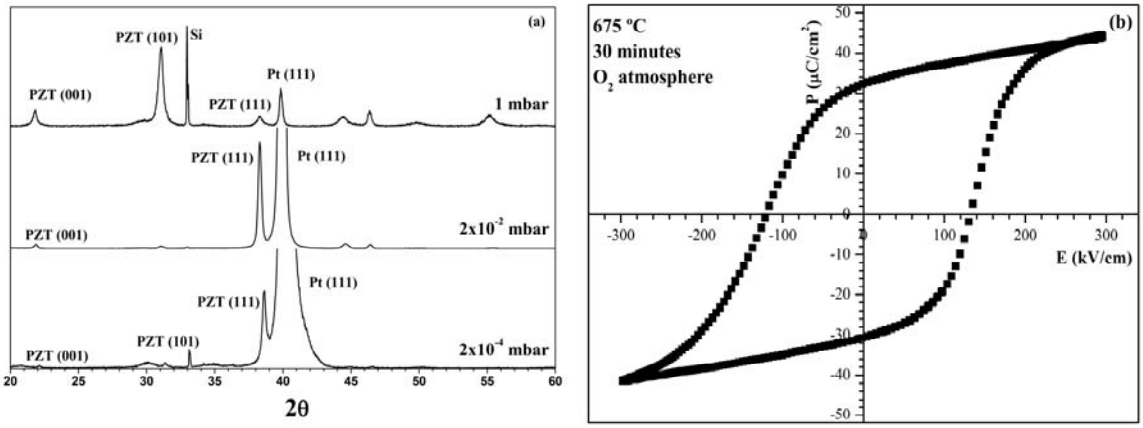

Figure 1: (a) X-Ray diffraction patterns for PZT thin films deposited with different O_2 pressure. (b) Ferroelectric hysteresis loop for a thin film heat treated in O_2 atmosphere at 675ºC for 30 minutes.

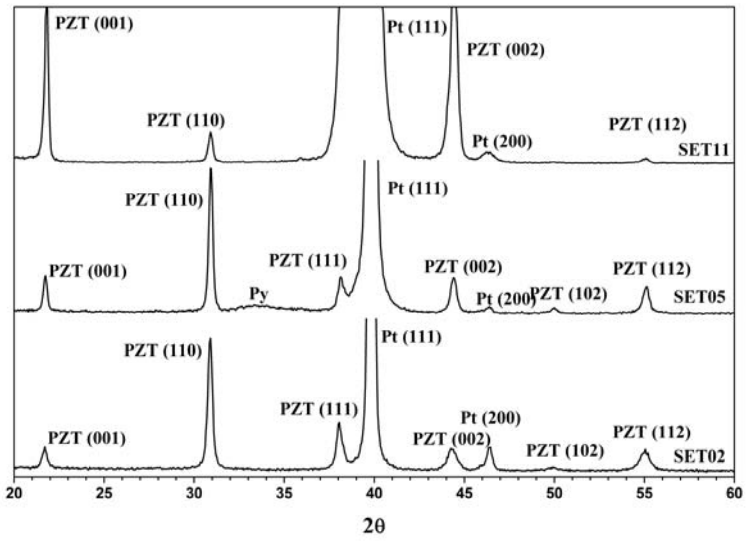

Figure 2: X-Ray diffraction patterns for PZT thin films deposited over different bottom electrodes.

It is known from the results reported for PZT films obtained by other techniques that the PZT crystallographic orientation depends on the processing parameters for the bottom electrodes [6]. Figure 2 shows the X-ray diffraction scans for PZT films deposited over electrodes made under different deposition conditions. The increase Pt deposition temperature did not affect the PZT orientation when the Ti films were deposited at room temperature; nevertheless, the preferred orientation became (001) instead of (110) for a simultaneous increase in the Ti deposition temperature. The different PZT orientations are the final result form a combination of different stress and diffusion process; the relative importance of each of these process depends not only on the deposition conditions and heat-treatment schedules used for the PZT films, but also on the deposition conditions used for the bottom electrodes [7]. In this particular case, the different stress levels and the nucleation and growth of the perovskite crystal lattice having particular orientations were most probably related to changes in the extent of Ti diffusion through the Pt grain boundaries during the deposition of the metallic films at different temperatures, as previously reported for PZT films made by RF magnetron sputtering [8].

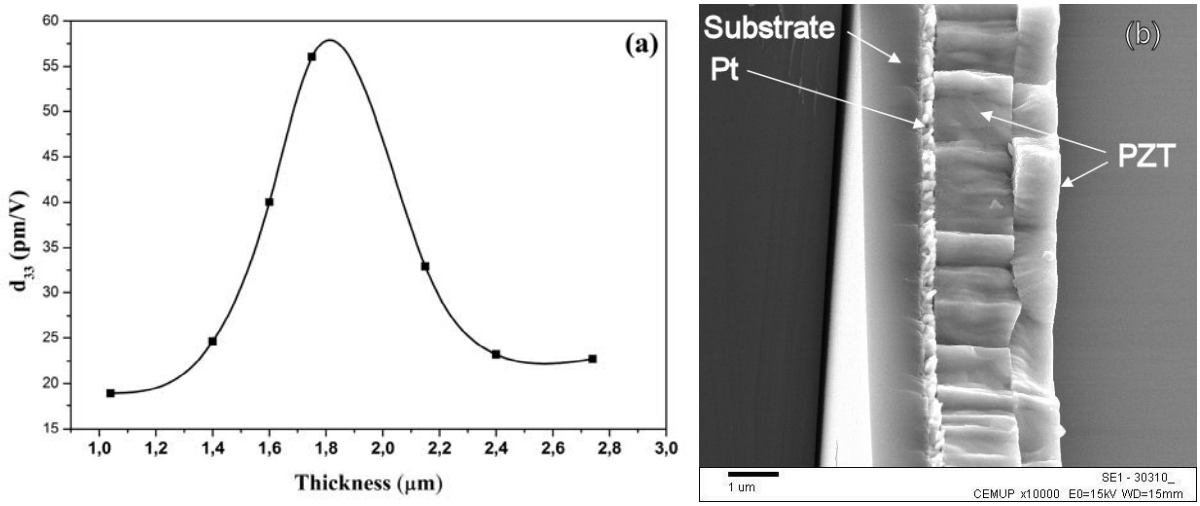

Figure 3: (a) Thickness dependence of the piezoelectric d_{33} coefficient. (b) SEM image from the cross-section of 2.4μm PZT film

In order to measure the piezoelectric d_{33} coefficient with a Michelson interferometer, top electrodes having high reflectivity and large area are needed. The larger electrode area increases the probability of having electrical shorts between the electrodes due to film defects, and this problem is more severe for thinner films. For this reason the thickness of the PZT films was increased by varying the deposition time between 60 to 180 minutes using the optimized deposition conditions (2×10^{-2} mbar pressure, SET11 substrates). The Al top electrodes used had an area of 2.5 mm^2. In order to avoid the measurement of the substrate deformation the samples were glued to a brass support and special care was taken to guarantee a homogeneous distribution of the extra strong adhesive across the substrate. In order to insure the accuracy of the results some samples were also measured with a double beam fiber interferometer that confirmed the values obtained [4].
Figure 3(a) shows the effect of film thickness on the d_{33} piezoelectric coefficient which increases up to a maximum value of 55 pm/V for films around 1.8 μm thick. For higher thickness the value of d_{33} decreases to approximately 20 pm/V. This dependence was not expected because this coefficient should not depend on the thickness of the piezoelectric layer [9]. Further SEM analysis has revealed the presence of two different layers for films with thickness above 1.8 μm, as shown in the film cross-section on figure 3(b). For these thick films the orientation is predominantly (110) but with strong (001) peaks. In order to investigate the possibility of an orientation change for the second layer, a sequence of small angle X-ray diffraction scans (from 1º to 5º incidence) were made. The results for a film with 2.4 μm thickness are shown in figure 4 together with a normal θ-2θ X-ray scan. The crystalline structure and the relative intensity of the peaks did not change across the film

thickness. This indicates that the development of the double layered structure is not related to any change in the crystalline orientation of the film. It should be pointed out that the thickness of first PZT layer, growing from the bottom electrode, is approximately equal to the thickness of the films having optimal values for the piezoelectric property measured (1.8 μm).

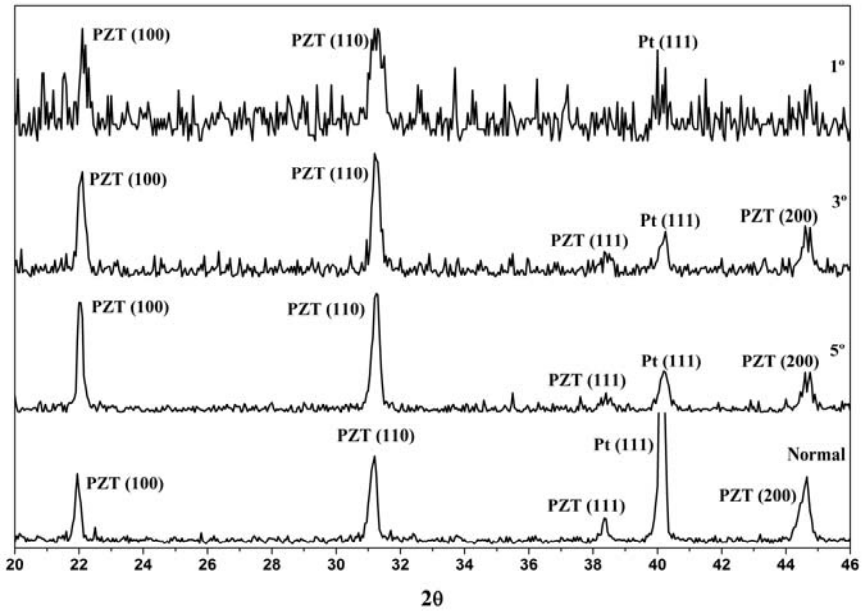

Figure 4: A comparison between a normal θ-2θ X-ray diffractogram an small angle X-ray diffraction scans for a 2.4 μm thick film.

Conclusions

In this article the laser ablation of PZT thin films, with Zr/Ti ratio of 52/48 onto platinized silicon substrates was studied. The processing conditions were changed in order to maximize the ferroelectric and piezoelectric properties. The best remanent polarization values (~30 $\mu C/cm^2$) compare favorably with those reported by Zhang et al [3]. The effect of the deposition conditions of the Ti and Pt sputtered layers on the PZT properties was investigated. The deposition temperature of the metallic films had a strong effect on the crystallographic preferred orientation of the PZT film. This was considered to arise from the residual stresses in the film. The values for d_{33} piezoelectric coefficient were measured using a Michelson interferometer. The maximum value for the d_{33} coefficient was 55 pm/V for a film thickness of approximately 1.8 μm. For thicker films, the formation of a double layer structure, with both layers having the same crystallographic orientation was observed. One possible explanation is an increase of mechanical stresses in the film with increasing thicknesses however further work is still needed in order to fully understand this phenomenon.

References

[1] S. Trolier-McKinstry, P. Muralt: Journal of Electroceramics, Vol. 12 (2004), p. 7
[2] S. Donati, L. Barbieri, G. Martini: IEEE Photon. Technol. Lett. Vol. 10 (1998), p. 1428
[3] L. Zhang et al: Jpn. J. Appl. Phys., Vol. 42 (2003), p. 3986
[4] S. Donati, L. Barbieri, G. Martini: IEEE Photonics Techonology Letters, Vol. 10 (1998), p. 1428
[5] J. R. Fernandes et al: Review of Scientific Instrumens, Vol. 72, (2002), p. 2073
[6] K. Aoki, T. Sakoda, Y. Fukuda: Jpn. J. Appl. Phys. Vol. 37 (1998). p. L522
[7] C. C. Mardare et al: Appl. Surf. Sci. Vol. 243 (2005), p. 113.
[8] H.-J. Nam, H.-H. Kim, W.-J. Lee: Jpn. J. Appl. Phys. Vol. 37 (1998), p. 3462
[9] L. Lian, N. R. Sottos: Journal of Applied Physics, Vol. 87 (2000), p. 3941