Characterization of sol-gel PZT films on Pt-coated substrates

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Abstract. A conventional sol-gel process was used to spin-cast PZT films on oxidized Si wafers coated with sputtered Pt layers. After annealing at 550 °C–800 °C, the resulting perovskite-type PZT films showed different textures and surface morphologies, depending on whether or not a Ti adhesion layer was used. If a Ti layer was present, Ti diffusion into and through the Pt film leads to a compound Pt_3Ti, which facilitates crystallization of the perovskite PZT phase; without Ti, crystallization is more difficult and occurs via the growth of dendritic crystallites. Several optical and electrical properties of the PZT films have been measured; the first results indicate high dielectric constants ($\epsilon \simeq 480$) and acceptable ferroelectric behaviour.

1. Introduction

In recent years, interest in thin films of perovskite-type materials like $PbZr_xTi_{1-x}O_3$ (PZT) has increased considerably because of applications in e.g. ferroelectric non-volatile memory devices and piezoelectrically driven microelectromechanical systems. An important topic of investigation is the choice of the electrode materials to be included in the conventional electrode-PZT-electrode sandwich design used in these applications. The choice of the electrode material is dominated by two aspects: (i) reactivity, and (ii) enhancement of oriented crystallization. Because of the high temperatures required during deposition or annealing of PZT, a chemically inert electrode material like platinum would be preferred to prevent reactions between constituents of the layer package. However, the results obtained with this and other metals are inconsistent, especially with respect to .ferroelectric fatigue. For this reason several authors have tried conducting oxides, like $La_{0.05}Sr_{0.5}CoO_3$ [1, 2]. Metals are still preferred in most applications, however, because of their much lower resistivities.

In this paper we shall discuss some of our results obtained with Pt electrodes. Because the adhesion of Pt layers on substrates like $Si-SiO_2$ or $Si-Si_3N_4$ is insufficient, an adhesion layer is generally required. Several metals can be used for this purpose, although Ti is the most popular. In this paper we shall extend our earlier work [3], which was focused on the structural implications of the use of a Ti adhesion layer, and present additional electrical and optical measurements on sol-gel PZT films on Pt-Ti coated substrates.

2. Experimental procedure

A conventional sol-gel process [4] (solution composition: Pb:Zr:Ti = 1.05:0.53:0.47) was used to spin-cast films on 3 inch Si substrates coated with thermal SiO_2, LPCVD Si_3N_4, DC-magnetron sputtered Pt, Ti, Cr, or combinations of these layers. The gel films were dried in air (20 min, 120 °C) and subsequently annealed in an oven in a pure O_2 flow, at temperatures between 400 °C and 850 °C; several different heating treatments were tried. One spinning plus annealing cycle leads to a PZT film with a thickness of around 60 nm; for thicker films multiple cycles were used. The PZT films were characterized with x-ray diffraction (XRD) with a Cu source, energy dispersive x-ray spectroscopy (EDX), Auger electron spectroscopy (AES), and ellipsometry (wavelengths: 632.8 nm and 1500 nm); dielectric constants and ferroelectric hysteresis loops of the films were measured on 1 mm^2 capacitors, using a network analyzer and a conventional Sawyer–Tower set-up, respectively.

3. Results and discussion

Figure 1 shows ellipsometer results (632.8 nm) for PZT layers on different substrates, resulting from a single spin-casting step, which after drying at 120 °C were annealed at subsequent temperatures of 400 up to 850 °C. Several effects can be observed: (i) the layers deposited on Pt(-Ti) continuously shrink during annealing, up to a factor of 3, while the refractive index increases up to 700 °C, and decreases slightly for still higher temperatures; the latter effect is probably due to Pb loss, as could be confirmed by EDX measurements;
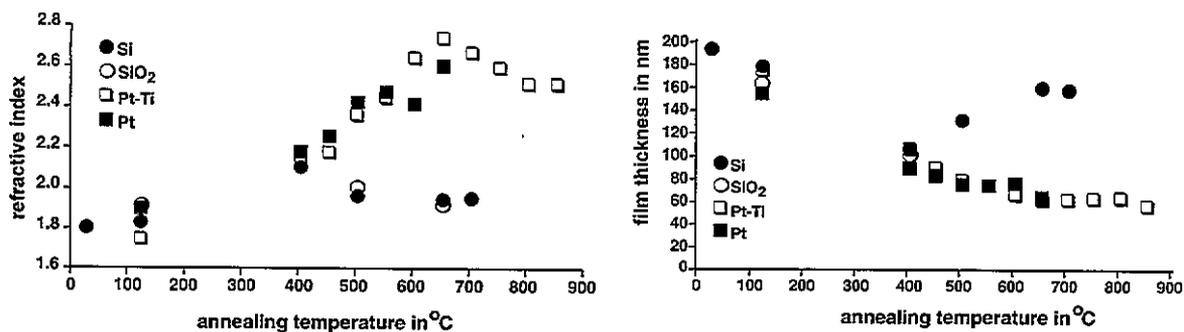
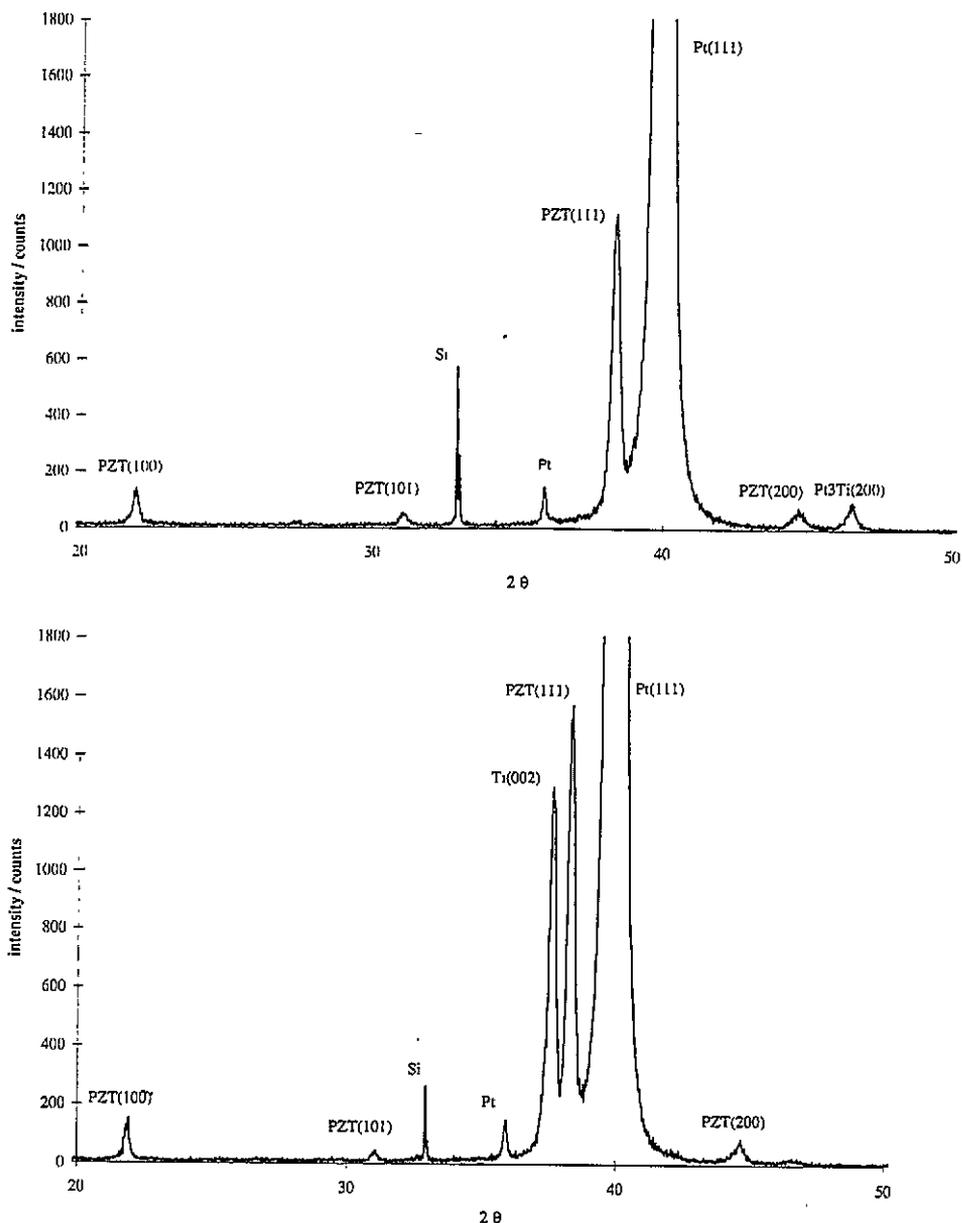**Figure 1.** Annealing results of PZT on Si, SiO₂–Si, Pt–SiO₂–Si and Pt–Ti–SiO₂–Si.

Figure 2. XRD spectra of PZT on Pt–Ti–SiO₂–Si; M8P (top) and M1N (bottom); see text.

(ii) the layers on Si and SiO₂ (and also on Si₃N₄, although not shown in the figure) shrink up to around 400 °C, and become thicker again for higher temperatures; the refractive index increases up to, and decreases above 400 °C; these effects are the result of a reaction of the PZT film with Si; this reaction prevents the crystallization of the perovskite PZT phase, as could be concluded from XRD measurements. The reaction also leads to cracks in the films, which do not occur in the films on Pt.

XRD results indicate that the structure of the PZT
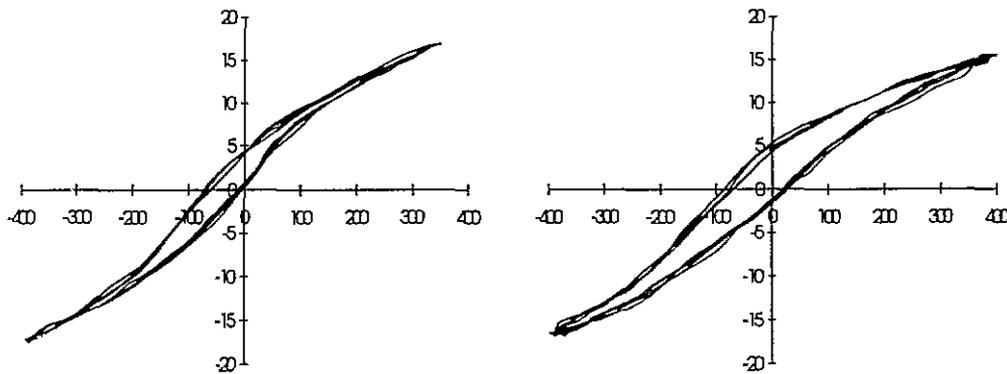
Figure 3. Ferroelectric hysteresis loops at 1 kHz for samples M8P (left) and M1N (right). Horizontal axis: electric field in kV cm^{-1}, vertical axis: polarization in μC cm^{-2}.

films on Pt (with or without Ti) is nanocrystalline pyrochlore for annealing temperatures up to around 500 °C; at that temperature faint perovskite-type PZT diffractions are observed, which become more intense at higher temperatures. The refractive index values in figure 1 agree with this trend in crystal structure development, considering reported values of 1.65 for pyrochlore and around 2.6 for sol-gel deposited perovskite PZT [5].

Figure 2 shows XRD spectra of around 200 nm thick, PZT films on Pt–Ti, resulting from 3 subsequent spin-casting cq annealing steps. Two different cycles were used: for sample M8P the process sequence was: spinning—20 min at 120 °C, 10 min at 700 °C, spinning, etc., while for M1N it was spinning—20 min at 120 °C, 20 min at 300 °C, 1 min at 700 °C, and again spinning. A lift-off process was used to deposit Al electrode patterns on top of the PZT layer. The only remarkable difference in the two XRD spectra is the presence of the α-Ti (002) peak at 38.22° for sample M1N, which for sample M8P is replaced by a small peak at 46.50°. The latter peak is due to Pt$_3$Ti {200} [3], which compound is the result of the diffusion of Ti into the Pt layer (as confirmed by AES measurements).

XRD measurements [3] show that PZT on Pt without Ti has a strong (101)/(011) texture, while in the presence of Ti the PZT layer has crystals with (100)/(010) or (111) faces parallel to the surface, as shown in figure 2; the relative occurence of the latter crystals varies from sample to sample, but a trend seems to be that more (100)/(011) is found on samples which were subjected to a higher thermal budget. One could argue that the Ti which diffuses through the Pt film precipitates close to the Pt surface (as indeed observed in AES) in a Pt$_3$Ti phase with (200) texture, on which PZT (100) grows epitaxially; similarly, as suggested by others [6], PZT (111) could grow epitaxially on Pt (111). The latter is however not in agreement with the texture observed for PZT on Pt without Ti.

Figure 3 shows ferro-electric hysteresis loops for the two samples on Pt–Ti. The sample obtained with the lowest thermal budget (M1N) shows a somewhat better loop. It

might be that this is a result of less Ti diffusion through the Pt film, although it is not clear what the effect of a Ti-rich interface on ferro-electric behaviour would be.

The dielectric constants of film M8P varied from 435 at the wafer edge to 510 at the wafer center. This variation is not caused by thickness non-uniformity, which is only 2%, but is probably due to a higher loss of Pb from the film at the wafer edges.

It would be interesting to compare the electrical properties of PZT films on Pt with and without Ti underneath. However, first attempts to do this failed because of a strongly decreased adhesion of the Pt film on SiO$_2$-coated Si after annealing, which resulted in blisters which penetrated through the PZT film and gave rise to electrical shorts between Al top and Pt bottom electrodes. Other adhesion layers for the Pt electrode are currently being tested.

Acknowledgments

References

[1] Ramesh B, Lee J, Sands T, Keramidas V G and Auciello O 1994 *Appl. Phys. Lett.* **64** 2511
[2] Dat R, Lichtenwalner D J, Auciello O and Kingon A I 1994 *Appl. Phys. Lett.* **64** 2673
[3] Gardeniers J G E, Elwenspoek M and Cobianu C 1994 Texture variations in sol-gel derived PZT films on substrates with platinum metallization *MRS Symp. Proc.* **343** p 451
[4] Udayakumar K R, Chen J, Krupanidhi S B and Cross L E 1990 *Proc. 7th Int. Symp. Appl. Ferroel. (Urbana-Champaign)* p 741
[5] Uhlmann D R, Teowee G, Boulton J M, Mokatef S and Lee S C 1992 *J. Non-Cryst. Solids* **147–148** 409
[6] Tani T, Xu Z and Payne D A 1993 *Ferroelectric Thin Films III, MRS Symp. Proc.* **310** 269