TEXTURE VARIATIONS IN SOL-GEL DERIVED PZT FILMS ON SUBSTRATES WITH PLATINUM METALLIZATION

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ABSTRACT

Metalorganic precursor solutions of composition Zr : Ti = 0.53 : 0.47 were used to spin-cast PZT layers on sputtered Pt films. After annealing at temperatures of 550 °C - 800 °C, the PZT films of tetragonal perovskite structure reproducibly showed different textures and surface morphologies, depending on whether or not a Ti layer was used as an adhesion layer for the Pt film. The texture differences were found to be independent of annealing treatment. It is argued that the observed texture differences are caused by a change in Pt-PZT interface composition, resulting from the diffusion of Ti into the Pt film during annealing; X-ray diffraction of an annealed Pt/Ti/SiO_2/Si film combination provided evidence for a compound Pt_3Ti. Annealing at 850 °C caused severe diffusion of Ti from the metal layer into the PZT film, leading to a tetragonal PZT layer with lattice constants corresponding to a Zr : Ti ratio of 30 : 70.

INTRODUCTION

In recent years the interest in thin films of perovskite-type materials like $PbZr_xTi_{1-x}O_3$ (PZT) has increased considerably because of the applications in e.g. ferroelectric non-volatile memory devices and piezoelectrically driven micro electromechanical systems. An important issue in the use of PZT films for these and other applications is the choice of the (bottom) electrode material. Because of the relatively high temperatures involved during deposition or annealing (500°C and higher) and the reactivity of PZT, interdiffusion of layers may occur, leading to undesired, irreproducible electrical changes in the films. Prevention of these effects demands the use of chemically inert materials like Pt, which, because of the inertness, in most cases also requires the addition of an adhesion layer (e.g. Ti). In some cases an additional diffusion barier is needed to prevent reaction of the metal package with the (silicon) substrate.

In this paper it will be shown that the use of Pt-Ti layer combinations has important implications for the structural properties (in particular the texture) of sol-gel PZT films. The experimental work will mainly consist of an X-ray diffraction (XRD) study, while additional information is gathered from scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX).

EXPERIMENTAL

A solution of organometallic precursors in 2-methoxyethanol with mole fraction ratios Pb:Zr:Ti = 1.05:0.53:0.47 and a total Zr + Ti concentration of 0.50 M was prepared, to which a mixture of HNO_3-H_2O-2-methoxyethanol was added as a catalyst for gel formation (final concentrations of HNO_3 and H_2O in the solution: $1.4\cdot10^{-3}$ M and 0.51 M, resp.). Preparations of the solutions were

Mat. Res. Soc. Symp. Proc. Vol. 343. ©1994 Materials Research Society

carried out as described by Udayakumar et al. [1]. After filtering, the solution was spin-cast (30 sec. at 2000 rpm.) on metallized substrates. The films were dried for 20 min. on a hotplate at 120 °C in air, and subsequently fired for 20 min at 400 °C in an oven in a flow of pure O_2. To promote crystallization of the films, a high temperature annealing step in pure O_2 was performed at a temperature between 400 °C and 850 °C; different annealing times and temperature ramping procedures were investigated. The substrates used were 3" thermally oxidized silicon wafers coated with either a Pt layer or a Pt layer with a Ti adhesion layer underneath. These metal films were deposited by DC magnetron sputtering from pure metal targets in Ar gas. Full details of the deposition and annealing of the metal films will be given elsewhere [2].

The PZT films were characterized with XRD, SEM, and EDX. Film thicknesses were determined with ellipsometry. XRD was performed with a Cu source; all diffraction angles 2θ mentioned in this paper are related to a wavelength of 0.154186 nm (CuKα). In all measurements the Si (004) substrate peak was found at a 2θ value of within 0.01° of the theoretical value.

RESULTS

Fig.1 shows XRD spectra of a 60 nm thick PZT film, resulting from a single spin-casting step on a substrate containing a Pt film on Ti. The film was fired at 400 °C for 20 min. and subsequently annealed at increasing temperatures up to 850 °C. Annealing at a particular temperature was performed for 30 min, while in between the annealing steps the samples were heated up and cooled down (to 25 °C) as fast as possible. The spectra show that after firing at 400 °C an amorphous film results. Crystallization does not occur below 500 °C; the corresponding spectrum shows faint PZT diffraction peaks at 22.0° and 44.8°, and somewhat stronger diffractions at 14.5°, 29.7° and 35.8°. The latter diffraction peaks correspond well with those expected for a pyrochlore-type oxide, $Pb_2(Zr,Ti)_2O_{(7-x)}$ [3,4]. The pyrochlore diffraction peaks remain visible until 650 °C. Their relative intensity with respect to those of the PZT diffractions decreases considerably in this temperature range. The film which results at 650 °C shows PZT diffractions for 2θ-values of 21.95°, 38.37° (this is not the exact value, since the peak is positioned on the "foot" of the Pt (111) peak at 39.91°) and 44.75°, corresponding to the (100)/(010), (111) and (200)/(020) diffractions, resp., of tetragonal PZT with lattice parameter a = 0.4049 nm. The literature value for a for the chosen Zr:Ti ratio of 53:47 is 0.4040 nm [5], which implies that the PZT film either is in a state of compressive stress (giving a strain of 0.23 % perpendicular to the film surface) or has a composition with a slightly higher Zr : Ti ratio (which was also found in the EDX measurements). In addition to these changes, it is observed that the α-Ti (002) peak, which is present in the spectra at 2θ = 38.22° at temperatures up to 600 °C, has disappeared in the spectra for temperatures of 650 °C and higher, while from 550 °C on a new diffraction peak is observed, at 46.50°.

Subsequent heating of the sample does not give structural changes in the PZT film, until a temperature of 850 °C is reached. At this temperature new diffraction peaks appear, at 22.46° and 45.88°, while the PZT (111) peak seems to have disappeared from the spectra; these peaks are probably due to a tetragonal PZT phase with a Zr:Ti ratio of 30:70. Furthermore, a broad diffraction peak arises at 30.47°, which is either due to a pyrochlore phase $Pb(Zr,Ti)_3O_7$ [4] or to yellow-PbO (002) [6]. Additionally, peaks due to TiO_2 (rutile) are observed at 27.50°, 36.19° and 54.48°.

Fig. 2 shows an XRD spectrum of a PZT film deposited on Pt without Ti adhesion layer, which was annealed at 700 °C (after the drying and firing steps mentioned before). It can be seen

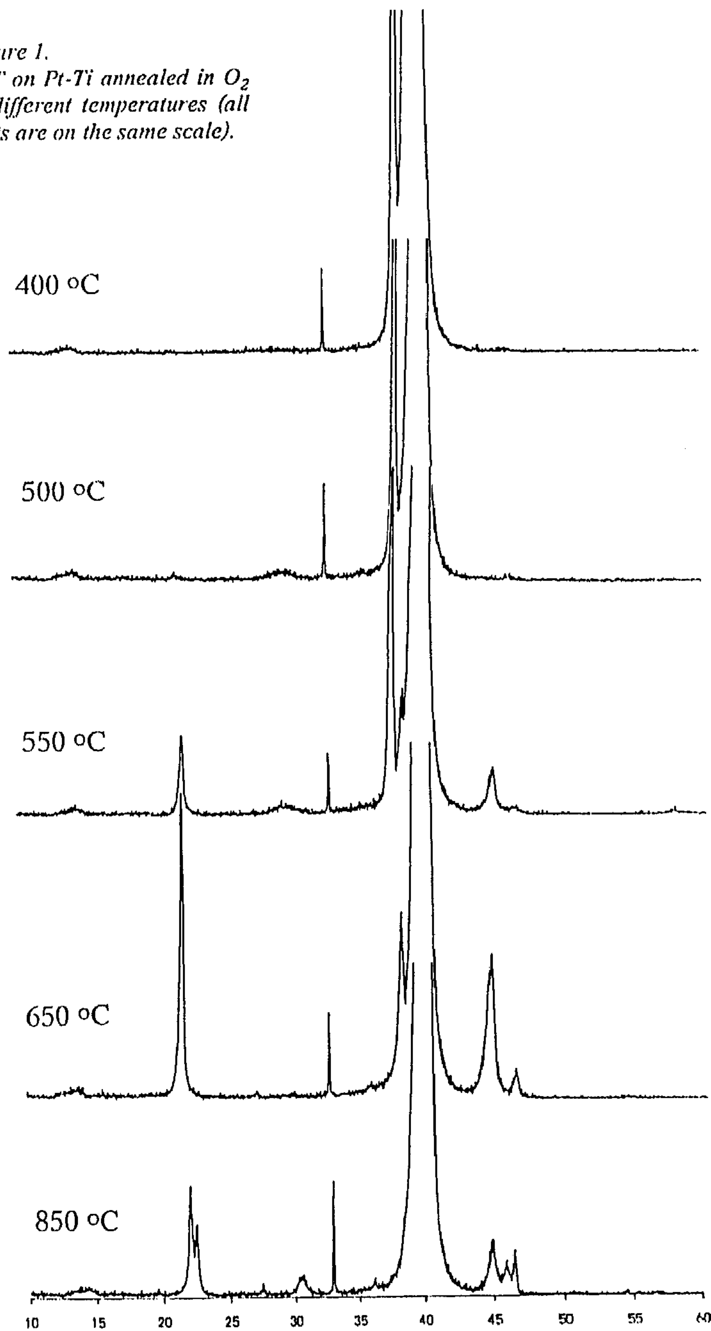
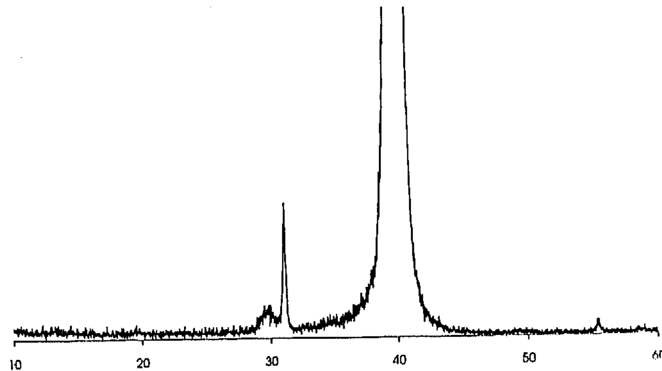


Figure 1.
PZT on Pt-Ti annealed in O_2 at different temperatures (all plots are on the same scale).

that the texture of this film is different from that in fig. 1: peaks are found for PZT (101)/(011) at 31.04° and for PZT (121)/(211) at 55.40°. At 29.48° a broad peak is found, which is probably due to pyrochlore (222).

Fig. 2.
PZT on Pt (without Ti) annealed at 700 °C



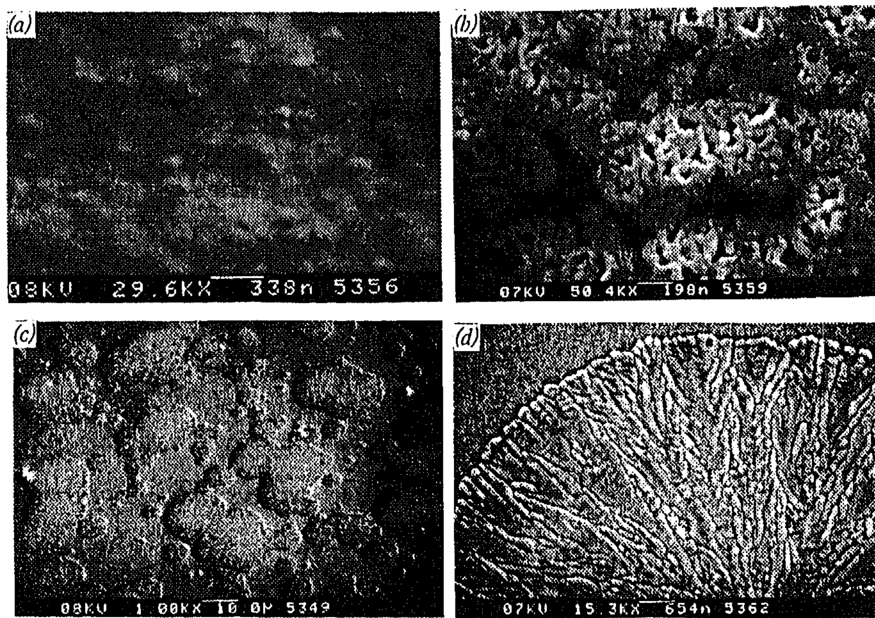


Fig. 3. SEM photographs of: (a) and (b) PZT on Pt with Ti; (c) and (d) PZT on Pt without Ti; films of (a), (c) and (d) were annealed in O_2 at 700 °C, (b) in O_2 at 850 °C; (d) is an enlarged view of part of (c).

The above-mentioned texture differences between PZT on Pt with and without Ti adhesion layer turned out to be reproducible, and independent of the heating treatment (annealing temperature and time, ramping procedures) of the films.

The surface morphology of the two films was also markedly different (fig. 3): a film on Pt without Ti shows the "rosettes" often encountered in PZT films crystallizing from an amorphous matrix [7], while a PZT film on Pt with Ti underneath shows a smooth surface. When the latter film was annealed at 850 °C, it became porous, probably because of extreme PbO evaporation.

Fig. 4 shows XRD spectra of Pt films, with and without Ti underneath, as-deposited and annealed at 700 °C in N_2. All Pt films show a pronounced {111} texture. Table 1 summarizes the results. After annealing, the XRD spectrum of Pt on Ti shows a diffraction at 46.56°, while the Ti (002) peak at 38.20° has disappeared. Although some authors have attributed the former peak to Pt(200) [8], we think that it must be due to the (200) planes of the alloy Pt_3Ti, which forms during annealing at temperatures at or above 550 °C (fig.1). The Pt (200) diffraction is expected at 46.44°, considering the 2θ value of 39.93° for Pt (111) in this film.; a peak position difference of 0.14° is significant, considering the experimental error of 0.02°.

Table 1. XRD results of as-deposited and annealed Pt films on Si-SiO_2.

sample	2θ Pt (111)	FWHM Pt (111)	2θ other	FWHM other
Pt, as-deposited	39.58°	0.36°	-	-
Pt, annealed	39.93°	0.15°	-	-
Pt-Ti, as-dep.	39.55°	0.38°	38.20°	0.40°
Pt-Ti, annealed	39.93°	0.18°	46.56°	0.35°

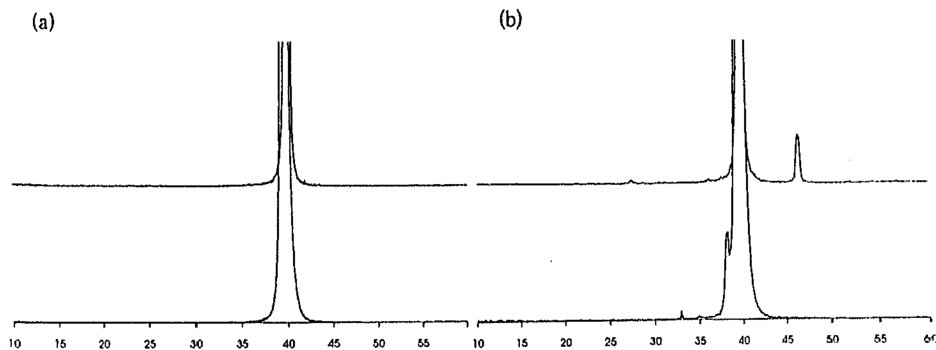


Fig.4. (a) Pt film; bottom: as-deposited, top: annealed at 700 °C; (b) Pt on Ti; bottom: as-deposited, top: annealed at 700 °C; all plots have the same vertical scale.

The XRD results indicate that as-deposited Pt films have a compressive residual stress (strain perpendicular to surface 0.53 %), which changes to tensile stress after annealing (perpendicular

strain 0.31 %); the decreased line widths indicate an increased grain size after annealing. No differences between Pt with or without Ti are found in this respect.

In agreement with other authors (e.g. ref. [8]), we have found evidence for the presence of TiO_2 (rutile) after annealing of our Pt-Ti-SiO_2-Si layer package, although the corresponding XRD peak at 26.85° has only a very low intensity with respect to the Pt and Pt_3Ti peaks.

DISCUSSION AND CONCLUSIONS

The results for PZT on Pt agree with those reported by others (e.g. refs. [4,7]): PZT crystallization is impeded, until at a temperature the already present nanocrystalline pyrochlore phase becomes so unstable with respect to PZT, that PZT nuclei are formed, which expand in an explosive fashion to fractal-like dendritic crystals ("rosettes"). It was observed that after a certain fraction of the film had crystallized, prolonged annealing did not give further growth of the rosettes; this is probably caused by PbO loss from the film, which impedes PZT crystallization. The higher Pb content of the rosettes with respect to the matrix was confirmed by EDX.

For PZT on Pt+Ti it was found that crystallization occurs readily, giving almost featureless films. XRD results indicate that in this case Ti diffuses into the Pt layer (giving a compound Pt_3Ti) and probably also through the Pt. At 850 °C this results in a film with two PZT phases: one with the expected ratio Zr:Ti = 53:47, and one with Zr:Ti = 30:70. We think that at lower temperatures (550 °C) a Ti-rich layer is formed at the Pt-PZT interface, which lowers the barrier for PZT nucleation and results in a high density of small crystallites in the film.

A remarkable observation was that after annealing at 850 °C the PZT (111) diffraction has disappeared. We think that this indicates that the nucleation layer on the Ti-rich interface is (111) oriented; on this layer new PZT crystals nucleate, which have (100) texture. When Ti diffusion becomes very severe, new (100)-oriented crystallites form at the expense of the (111)-oriented initial layer.

ACKNOWLEDGEMENTS

The authors thank B. Otter for SEM and EDX measurements, J. Sanderink for sputtering depositions. C. Cobianu acknowledges the support of the EC-program "TEMPUS" and wishes to thank profs. J. Fluitman and D. Dascalu for their efforts in establishing the joint research project.

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