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Effect of the substrate heterostructure on the texture of lanthanum modified lead titanate thin films

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Abstract

Modified lead titanate thin films with a nominal composition of $Pb_{0.88}La_{0.08}TiO_3$ (PTL) have been prepared by chemical solution deposition (CSD) onto annealed Ti/Pt/Ti/(100)Si and Pt/TiO_2/(100)Si. Composition and heterostructure of the PTL films on the two substrates have been studied by Rutherford backscattering spectroscopy (RBS). Composition of the PTL films on the two substrates is similar and close to the nominal one. However, the Ti/Pt/Ti/(100)Si and Pt/TiO_2/(100)Si substrates induces different textures in the PTL films. The films on Ti/Pt/Ti/(100)Si developed a $<111>$ preferred orientation, whereas the films on Pt/TiO_2/(100)Si have a $<100>$ $<001>$ mixed preferred orientation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Films; Perovskites; Pyroelectric properties; Sol–gel processes

1. Introduction

Microelectronic devices including ferroelectric ceramic thin films integrated with silicon substrates have created much interest during the last years due to the use of their ferroelectric, piezoelectric and pyroelectric properties at microscale level.[1] Pure and modified lead titanate perovskites (PT and modified-PT) are now being considered as promising materials for these applications, specially in pyroelectric sensors and micro-electro-mechanical systems (MEMS).[2] Performance of these materials into these devices is even better than that of the classical PZT films, since they have high enough spontaneous polarization and lower dielectric permitivities than PZT.

The piezo and pyroelectric properties of these films strongly depend on their texture, which is determined by the substrate and processing conditions.

We present here a Rutherford backscattering spectroscopy (RBS) study that aims to understand the effect of different silicon based substrates on the growth of chemical solution deposited (CSD) lanthanum modified lead titanate (PTL) thin films.

2. Experimental procedure

PTL thin films were prepared by CSD onto two types of substrates: Ti/Pt/Ti/(100)Si and Pt/TiO_2/(100)Si. Pt, Ti and TiO_2 layers were deposited by rf-magnetron sputtering on (100)Si substrates spontaneously oxidised in air. The Ti/Pt/Ti/(100)Si substrate was subjected to a thermal treatment in air at 650°C for 1800 s, with a heating rate of 10°C/min, previous to the deposition of the film, whereas the other substrate, Pt/TiO_2/(100)Si, was used as-obtained for the deposition of the films.

Films were spin-coated from a sol–gel solution[3] with a concentration of ~0.5 mol/l and a nominal composition of $Pb_{0.88}La_{0.08}TiO_3$ plus a 10 mol% excess of PbO. Wet layers were dried on a hot plate at 350°C for 60 s and crystallized in air by RTP at 650°C for 50 s, with a heating rate of ~30°C/s. Deposition, drying and crystallization were carried out 1–6 times on each substrate.

Cross-sections of the crystalline films were observed by scanning electron microscopy (SEM).

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Crystalline films and substrates were analysed by Rutherford backscattering spectroscopy (RBS). Films analysed by RBS were the two PTL films prepared on the two types of substrates (three-layer films), two bare Ti/Pt/Ti/(100)Si substrates, one as-prepared by sputtering and the other after annealing in air at 650°C for 1800 s, with a heating rate of 10°C/min, and a single-layer PTL film on the annealed Ti/Pt/Ti/(100)Si substrate. The RBS analyse were carried out with a 3 MV Tandem accelerator, using a 5.9 MeV (for the three-layers films) or a 1.9 MeV (for the ~100 nm thick film and the bare substrates) $^4He^{++}$ beam with the surface barrier detector set at 165°. High energy RBS was used to get a good resolution and the separation of the signals of the heavy elements.[4] The spectra were taken at the tilt angle of 0° (beam perpendicular to the sample surface). The RBS experimental data were analysed using the RUMP simulation code.[5] Error in the calculation of the composition was ~10%. A bulk density of the PTL layer of ~7.7 g/cm^3 and of the Pt of ~21.4 g/cm^3 were considered for the calculation of thicknesses. A roughness of ~100 Å at the PTL/Pt surface was considered in the simulation to get the best fit.

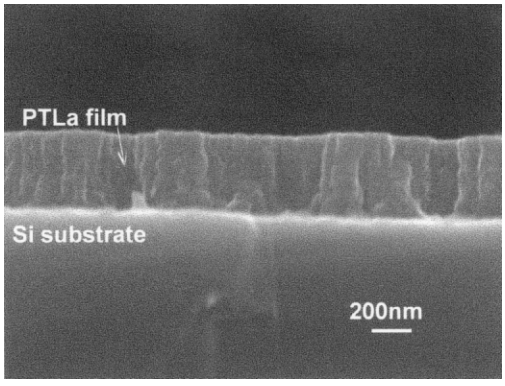

Fig. 1. SEM images of a cross-section of the 6-layer film on annealed Ti/Pt/Ti/(100)Si substrate.

3. Results

The thicknesses calculated from the cross-sections SEM images for the 3-layers films on Ti/Pt/Ti/(100)Si and on Pt/TiO_2/(100)Si were ~338 and ~335 nm, respectively. A columnar growth is observed in the cross-section image of a 6-layer film on Ti/Pt/Ti/(100)Si (Fig. 1). No preferred growth was observed in the films on Pt/TiO_2/(100)Si.

Figs. 2a and b shows the RBS experimental spectra and the simulations of the 3-layer PTL films on the two substrates. The ratios Pb/Ti and La/Ti of both films deduced from the simulations of the experimental RBS spectra are 0.93 and 0.07, respectively. These ratios are close to those of the nominal composition, $Pb_{0.88}La_{0.08}TiO_3$, taking into account the error of the measurement, ~10%. Thickness of the PTL layers calculated from RBS is similar for both films, ~250 nm. This thickness value is lower than that calculated from the SEM cross-sections images of the films. This is due to the assumption for the RBS calculations of a bulk density of the film equal to that obtained from the lattice parameters of the perovskite where the possible existence of porosity is not considered.

Heterostructures of the materials deduced from these analyses are depicted in the insets. It has to be noted that neither the Ti bottom layer of the Ti/Pt/Ti/(100)Si substrate nor the Ti top layer are distinguished in the spectrum of Fig. 2a. The signal of the latter is overlapped by the Ti signal of the PTL film which makes it difficult to determine the state of this layer. However, the Ti bottom layer would give a clear separated signal if present. This is the case for the PTL film on Pt/TiO_2/(100)Si with the two separated Ti signals of the Fig. 2b. The Ti signal appearing at higher energies corresponds to the Ti from the PTL film whereas the other Ti signal comes from the TiO_2 layer of the substrate. A Pt signal at the surface of the film is observed in the spectrum besides the Pt signal of the Pt bottom electrode. This is because the PTL film on Pt/TiO_2/(100)Si analysed by RBS had top Pt electrodes deposited.

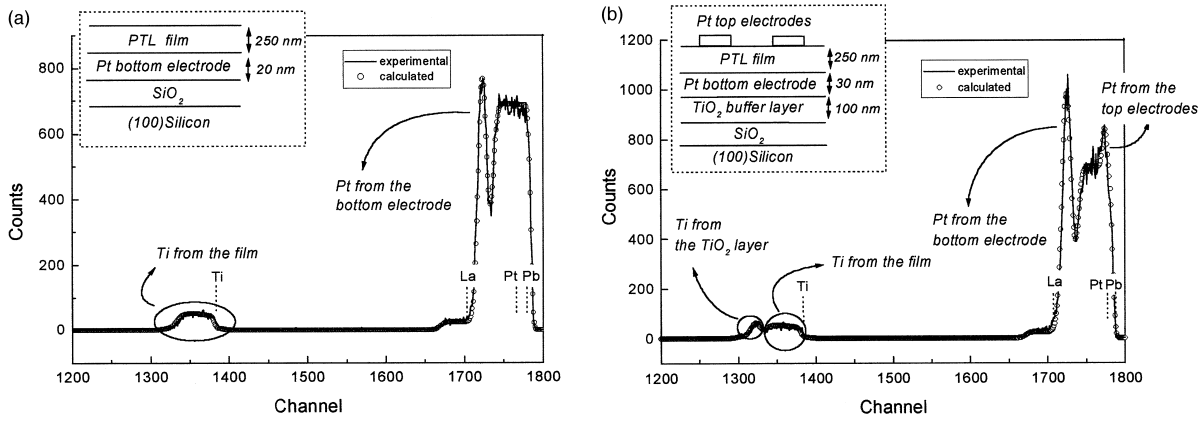

Fig. 2. RBS experimental spectra and simulations of the 3-layer PTL film on (a) Ti/Pt/Ti/(100)Si and (b) Pt/TiO_2/(100)Si. Insets show the heterostructures of the materials deduced from these spectra.

The Ti/Pt/Ti/(100)Si substrate was analysed by RBS as-prepared by rf-sputtering, after its annealing at 650°C and after the deposition on it of a layer of PTL with a thickness of ~100 nm. Fig. 3 shows the experimental RBS spectra and the simulations. The insets show the detail of the experimental spectra where the Ti signal appears.

Fig. 3a shows that the RBS spectra of the as-prepared substrate has a signal from the thin layer of Ti deposited on the Pt surface. The analysis indicates that this Ti layer is probably oxidized, since it is well simulated as TiO_2. The thicker layer of Ti under the Pt is also detected. The thickness of the top Ti layer increases and the thickness of the Ti layer under the Pt decreases when this substrate is subjected to the annealing at 650°C previous to the deposition of the PTL film (Fig. 3b).

A thin Ti layer under the Pt is still detected when a 1-layer thin PTL film is deposited onto the annealed substrate (Fig. 3c). However, as shown above (Fig. 2a), this Ti layer totally disappears when a thicker PTL film is prepared (~300 nm). The Ti top layer of the substrate cannot be distinguished from the Ti signal of the PTL film, neither in the PTL 1-layer film, of ~100 nm, nor in the 3-layer one, of ~250 nm.

4. Discussion

From the orientation distributions deduced from the quantitative texture analysis of the films, it was previously reported[6] that the films deposited on the Ti/Pt/Ti/(100)Si show a preferred <111> orientation, with smaller texture components along <001> and <100>. But the ones deposited on Pt/TiO_2/(100)Si had a mixed <100> <001> preferred orientation[6]. It was also measured a higher value of the pyroelectric coefficient for the PTL film onto Ti/Pt/Ti/(100)Si, $\gamma_s = 18.0\times10^{-9}$C cm^{-2} K^{-1}, than for the film onto Pt/TiO_2/(100)Si, $\gamma_s = 5.4\times10^{-9}$C cm^{-2} K^{-1}.

The mechanisms through which tetragonal PZT thin films prepared by CSD grow with a preferred <111> orientation on platinized silicon substrates have been widely discussed by different authors.[7–11] Experimental results have shown that non-textured PZT films are obtained on Pt, even if Pt has a high degree of (111) texture[7] and in spite of the close lattice mistmatch between the cubic Pt and the PZT. So, other explanations have been discussed. Tani et al[8] suggested that the <111> preferred orientation of the film appeared when the substrate contained some Ti at its surface. This

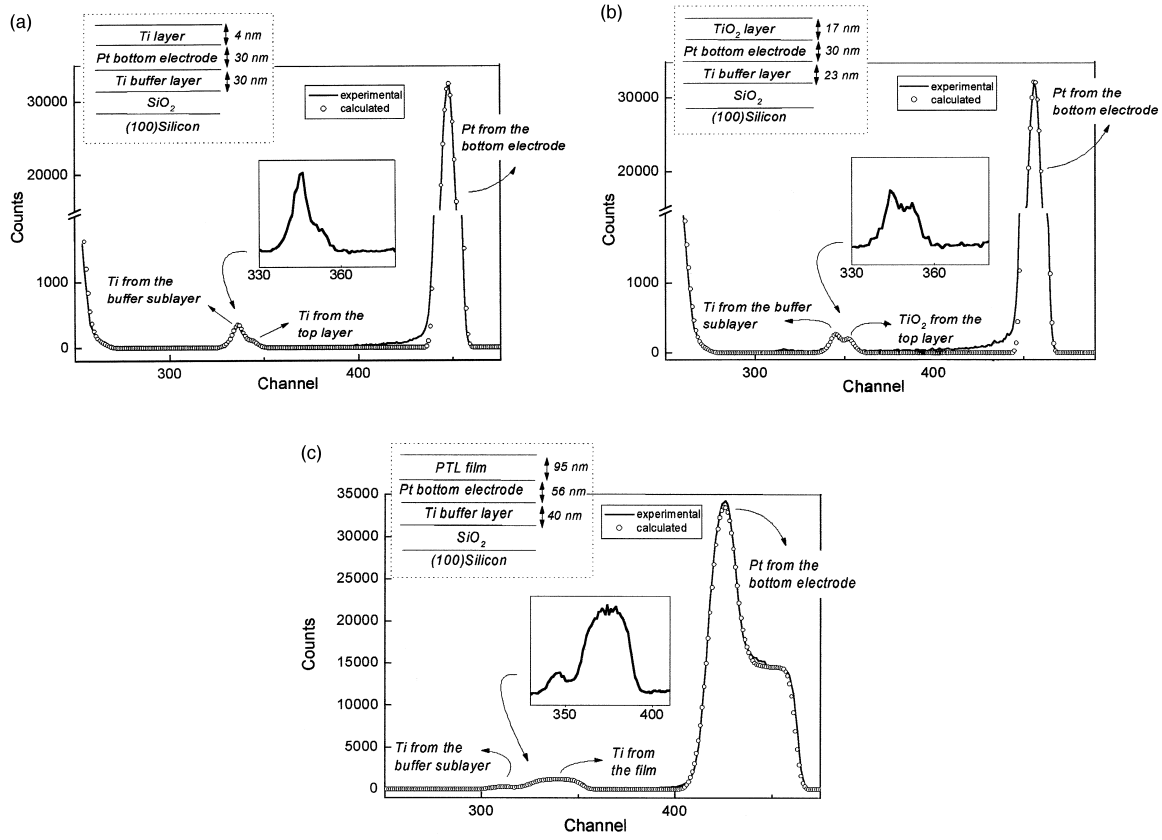

Fig. 3. RBS experimental spectra and simulations of (a) the as-prepared Ti/Pt/Ti/(100)Si substrate, (b) the Ti/Pt/Ti/(100)Si substrate annealed at 650°C and (c) a ~100 nm thick 1-layer PTL film onto the annealed Ti/Pt/Ti/(100)Si. Insets show the corresponding heteroestructures and the detail of the experimental spectra for the interval in which the Ti signal appears.

promotes the formation of an intermetallic Pt_3Ti cubic phase with a close lattice match with the tetragonal PZT. S.Y. Chen et al.[9] and Z. Huang et al.[10] indicated that $<111>$ textured PZT films are nucleated by an intermediate Pt_xPb layer formed at the surface of the substrate during annealing. Formation of the Pt_xPb is facilitated by an excess of lead, the annealing in a reducing atmosphere or a rapidly heating of the film. Finally, Muralt et al.[11] showed the efficiency of a thin TiO_2 layer on the Pt to obtain PZT films with a $<111>$ preferred orientation. They suggested that TiO_2 incorporates to the first layers of PZT, leading to slightly TiO_2 enriched PZT nuclei that facilitate the preferred growth of the film.

From Figs. 2a,3a, b and c, it is deduced that, during the thermal treatment, the Ti under the Pt electrode moves towards the surface and there it oxidizes. Simulation of a TiO_2 phase at the surface of Pt fits well to the experimental data. This Ti is not detected in the RBS curves of the film of Fig. 2a. It seems to indicate that Ti has totally migrated to the surface of the Pt. We cannot assure from this RBS study that the Ti has incorporated as TiO_2 to the first layers of the PTL perovskite promoting the $<111>$ orientation of the film onto Ti/Pt/Ti/(100)Si, as suggested by Muralt et al.[11] for PZT films. However, it is clear that this Ti layer has an important effect on the preferred growth of the film, since the same film onto Pt/TiO_2/(100)Si does not develop this texture.

The occurrence of the other mechanisms above indicated promoting the $<111>$ texture of the PTL films are not rejected here. Actually, we have previously reported the epitaxy between the Pt_3Ti phase and a modified lead titanate perovskite.[12] This lattice match would be enough for the preferred $<111>$ growth of the $Pb_{0.88}La_{0.08}TiO_3$ thin films on the Ti/Pt/Ti/(100)Si substrate. The RBS analyses clearly indicate that the Pt bottom electrode of this substrate is not contaminated by Ti. Simulations with an electrode containing Pt and Ti do not fit well to the experimental RBS curves of Figs. 2a, 3a, b and 3c, therefore, the Ti that migrates from the buffer sublayer goes all the way to the surface and could form the transient Pt_3Ti phase, since during film crystallization the conditions are different to the highly oxidizing one during the substrate annealing . The possibility of the formation during the annealing of the film of the intermediate Pt_xPb cannot be obviated either. But, the two PTL films, on Ti/Pt/Ti/(100)Si and on Pt/TiO_2/(100)Si, were prepared under the conditions described in the literature as favouring the formation of the Pt_xPb. However, only the former film developed the $<111>$ orientation.

5. Conclusions

PTL films were grown by CSD on Ti/Pt/Ti/(100)Si and Pt/TiO_2/(100)Si substrates, developing a $<111>$ and a mixed $<001>$, $<100>$ preferred orientations, respectively. The former is responsible of the spontaneous pyroelectricity of these films ($\gamma \sim 20\times10^{-9}$ C cm^{-1} K^{-1}).

RBS studies on 3-layer films on both types of substrates gave experimental confirmation of the films nominal composition. The Ti in the buffer sublayer of the Pt/TiO_2/(100)Si substrate was clearly separated from the Ti of the film. However, neither the Ti at the surface nor below the Pt were detected in the film on annealed Ti/Pt/Ti/(100)Si substrate.

RBS studies on the Ti/Pt/Ti/(100)Si substrate aimed to understand the effect of the Ti on the top on the development of the $<111>$ orientation of the PTL films on these annealed substrates. Experimental evidence of the (a) migration of the Ti in the buffer sublayer to the top of the Pt, (b) lack of Pt contamination by Ti and (c) oxidation of the Ti on the top of the Pt. RBS study of the 1-layer film shows still a remanence of Ti in the buffer sublayer.

The initial presence of oxidized Ti on the top of the substrate heteroestructure seems to play a role in the occurrence of the $<111>$ texture. However, during the film crystallisation, conditions are different from the oxidizing one at the annealing of the substrate and it cannot be rejected the hypothesis of the formation of Pt_3Ti. This could occur by migration of the remanent Ti that was observed in the buffer sublayer of the substrate after annealing, which provides a good lattice matching between the (111)Pt of the substrate and the (111) PTL perovskite.

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