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Citation: J. Appl. Phys. 96, 5691 (2004); doi: 10.1063/1.1805731
View online: http://dx.doi.org/10.1063/1.1805731
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La$_{0.8}$Sr$_{0.2}$MnO$_3$-heterostructure effects on the dielectric properties of PbTiO$_3$-based thin films

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(Received 7 June 2004; accepted 16 August 2004)

The present paper deals with substrate heterostructure effects on the microstructure and dielectric properties of Sm, Er, and La doped lead titanate (PT) thin films. The substrate heterostructures chosen include Si/(La$_{0.8}$Sr$_{0.2}$)MnO$_3$, (LSMO), Y-stabilized zirconia (YSZ)/LSMO and Si/Pt. Both LSMO and PT thin films were processed via chemical solution deposition. The results are compared to those of Sm and Er doped lead-zirconate-titanate (PZT). It is shown that the dielectric properties, and particularly the ferroelectric-to-paraelectric transition temperature of PT, are strongly affected by the substrate heterostructure. In comparison to PT on platinized Si, the transition temperature is shifted by more than 100$^\circ$C towards lower values in the case of Er and Sm doped PT on LSMO, while those of La doped PT and PZT are not affected at all. X-ray photoelectron spectroscopy investigations show a substantial interdiffusion between LSMO and PT. Particularly the diffusion of La towards the ferroelectric film and that of Pb towards LSMO are made responsible for the change in the dielectric properties. In the case of PZT we stipulate the formation of a stable pyrochlore diffusion barrier layer. © 2004 American Institute of Physics. [DOI: 10.1063/1.1805731]

I. INTRODUCTION

It is well known that substrate heterostructure decisively affects the microstructure and properties of PbTiO$_3$-based ferroelectric thin films. Mismatch in the thermal expansion and lattice parameters are known to control stress state, texture, and therefore ferroelectric and other functional properties of the films. In the case of PbZrO$_3$-PbTiO$_3$ solid solution (PZT) it is well known that the choice of the substrate heterostructure dramatically influences the fatigue resistance (resistance to change in the remnant polarization on electrical cycling) of the films. Particularly, it has been shown that conducting oxides of the perovskite-type structure such as (La$_{1-x}$Sr$_x$)CoO$_3$ and (La$_{1-x}$Sr$_x$)MnO$_3$ (LSMO) can lead to improved fatigue properties of PZT thin films via annihilation of oxygen vacancies at the ferroelectric/electrode interface. McNally, Kim, and Lange made use of chemical solution deposition (CSD) to process LSMO/PZT/LSMO heterostructures. Their results show that it is possible to obtain PZT films “with excellent polarization and fatigue behavior.” However, effects on the dielectric properties as well as interfacial reactions, which might be expected because of the high reactivity inherent to CSD films, were not investigated.

Rare-earth manganites with hole doping constitute an interesting class of conductive, ferromagnetic oxide materials. They exhibit colossal magnetoresistive properties which make them potential candidates as sensors and memory materials. Particularly LSMO is attracting growing attention because its Curie temperature can be adjusted to relatively high values via variation of the Sr concentration. For instance the Curie temperature of (La$_{0.8}$Sr$_{0.2}$)MnO$_3$ amounts to $\approx$390 K. The use of LSMO as electrode material for ferroelectric films may lead to a different class of multifunctional heterostructures with unusual properties. Grishin, Khartsev, and Johnson reported that it is possible to grow epitaxial heterostructures of LSMO and PZT and showed both ferroelectric and magnetoresistive properties of such heterostructures. In the present work, the properties of CSD heterostructures of LSMO and PbTiO$_3$-based films are reported. The effects of LSMO on the structure, ferroelectric, dielectric, and pyroelectric properties are being investigated. The substrates used were either (100)-Si or (110)-YSZ (Y-stabilized zirconia) monocrystals. The results are compared to those obtained on platinized silicon substrates.

II. EXPERIMENT

The precursor solution for (La$_{0.8}$Sr$_{0.2}$)MnO$_3$ has been prepared at room temperature from La-nitrate, Sr-nitrate, and Mn-acetate. First Mn-acetate was dissolved in a mixture of acetic acid and water, followed by dissolution of La- and Sr-nitrate. The precursor solutions of lanthanide elements (Ln) doped lead titanate ([Pb$_{1-x}$Ln$_x$]TiO$_3$ (PLnT) where Ln denote La, Er, or Sm) with a doping level $x$ of 5 mol% for Er and Sm and from 5 to 10 mol% for La were prepared using the procedure described in previous work, and shown schematically in Fig. 1.
Four layers of LSMO were spin coated on the substrate to give a final LSMO thickness of \(~200\) nm. Each layer was dried on hot plate at \(350^\circ\)C for \(10\) min before next coating, and final annealing at \(800^\circ\)C for \(20\) min was found to lead to full crystallization of the LSMO films. Six layers of PLnT were then spin coated with intermittent drying following the same scheme as above. Final annealing was conducted at \(700^\circ\)C for \(10\) min. For comparison, six layers of PLnT films were deposited on commercial platinized silicon wafers (Si/\text{SiO}_2/\text{Ti/Pt}) (Inostek, Seoul, Korea) under the same conditions. In the following, the specimens are designated PET5 for Er doped, PST5 for Sm doped, and PLT for La doped PbTiO\(_3\) films.

For x-ray photoelectron spectroscopy (XPS), two sets of specimens were processed. One specimen consisted of one layer of PET5 deposited on LSMO and annealed under the same conditions as above. The second specimen consisted of a PET5 bottom layer and a LSMO top layer. These configurations allow possible interdiffusion phenomena to be explored with a minimum of depth profiling, and thus allow undesirable artefacts due to preferential sputtering and redeposition to be avoided.

Phase composition was explored by means of x-ray diffractometry (XRD) in \(\Theta-2\Theta\) and grazing incidence (GI, grazing angle \(2^\circ\)) configurations (Seifer powder diffractometer, monochromated CuK\(_\alpha\) line \(\lambda=1.5418\) Å). Microstructural studies were performed by means of scanning electron (SEM, Philips XL30) and atomic force microscopy (AFM, nanostation SIS, Germany). The scanning probe imaging processor (version 2.3, image metrology) software was used to determine the mean grains diameter and root mean square roughness of the specimens. For analysis of LSMO/PLnT interface XPS (Omicron, Germany) was performed on the specimens described above at a high vacuum of \(10^{-9}\) m bar using an MgK\(_\alpha\) soft x-ray source.

For electrical measurements, capacitors were obtained by sputtering round Pt top electrodes of \(600\) \(\mu\)m diameter through a shadow mask and appropriate electrical contact to the bottom electrode.

The small signal dielectric properties were obtained on a computer controlled impedance analyzer (Agilent 4192A) equipped with a heating stage. A modulation voltage of 50 mV peak-to-peak was used in the frequency range from 100 Hz to 100 kHz. The ferroelectric transition temperature was obtained at a frequency of 1 kHz from the temperature dependence of the dielectric constant upon cooling from high temperature (500°C). The ferroelectric properties (polarization vs voltage \(P-V\) curves) were measured by means of a commercial ferroelectric testing system (RT6000S, Radiant Technologies, Albuquerque, USA).

### III. RESULTS

#### A. Microstructures

AFM micrographs of LSMO on Si and YSZ are illustrated in Fig. 2 where very small grains with a grain size in the range from 30 to 80 nm can be seen. In the case of Si substrate, the growth of the crystallites seems to occur on preferential sites, and this leads to grain agglomerates and somewhat high surface roughness with a rms value of 4.7 nm. Deposition on YSZ leads to more homogeneous microstructure with a rms roughness of 1.4 nm.

Figure 3 shows the corresponding XRD diffraction patterns where it can be seen that the film is fully crystallized with a random orientation of the grains. In fact additional experiments on commercial powder show the same reflections (see inset). The same patterns were obtained for LSMO deposited on YSZ monocrystals (not shown).

Smooth and fine grained surface morphologies with a grain size in the range from 50 to 80 nm were obtained for all PLnT films deposited on LSMO. This is exemplified in Fig. 4(a), which shows an AFM micrograph of PET5 on YSZ/LSMO. In Fig. 4(a) the surface topography of PET5 on
platinized Si is also shown for comparison, where it can be seen that a somewhat larger grain size is obtained.

The XRD patterns of the films deposited on LSMO show regardless of doping and substrate type (Si or YSZ) a polycrystalline microstructure with no strong preferential orientation, Fig. 5. This contrasts with the films deposited on Pt, which have the tendency to develop (100)/(111) textures with, however, strong (111) texture for PET5 films, Fig. 5(b). It can also be seen that the films deposited on Pt show the presence of a peak in the vicinity of 30°(2θ) which is attributed to the lead deficient, nonferroelectric pyrochlore phase (probably Pb,Ln)2Ti2O7−δ where Ln denote either Er or Sm). It must be pointed out that this peak is not present in the usual Θ-2Θ diffraction patterns, which suggests that pyrochlore is probably present at the surface.

### B. Ferroelectric properties

Well-developed hysteresis loops could be obtained for all films investigated at the exception of PET5 on Si/LSMO, which was found to be conductive. Figure 6(a) shows the dependence of the P-E curves of PST5 on different substrates. The ferroelectric properties are quite similar, although it can be seen that PST on Si/LSMO is characterized by higher remnant polarization associated with somewhat lower coercive field. In contrast, the results obtained on PET5 show a stronger dependence of the ferroelectric characteristics on the substrate as evidenced in Fig. 6(b). A square hysteresis loop is obtained on YSZ/LSMO with remnant polarization and coercive field twice as high as on Pt bottom electrode. YSZ/LSMO appears therefore to affect dramatically the ferroelectric properties of PET5. Since the ferroelectric properties are intimately related to domain switching capabilities, it is presumed that this substrate type leads to better domain switching behavior (see below for discussion).

### C. Dielectric properties

The frequency dependence of the dielectric constant ε’ and loss tangent tan δ can be seen in Fig. 7. Both properties are strongly affected by the substrate type. For PET5 the dielectric constant is much lower on LSMO, and above 10 kHz it shows an abrupt decrease, while tanδ rises expo-
nentially. It is believed that this behavior arises as a result of the higher contribution of the series resistance of the LSMO electrode to the impedance properties at higher frequencies.\(^{12}\) In the case of PST5, the films on LSMO are characterized by a higher dielectric constant, which probably is the result of the more pronounced (001)/(100) texture of the film, Fig. 7(b). The frequency dependence of the dielectric properties is, however, very similar to that observed for PET5. Table I summarizes the dielectric properties obtained at 1 kHz. The properties of PLT10 on Pt and LSMO are also listed for comparison. As expected,\(^{13}\) higher \(\varepsilon'\) and \(\tan\delta\) are obtained for PLT10. Deposition of PLT on LSMO results in a much higher dielectric constant (these results are reported here only for the sake of comparison. They will be described and discussed in detail elsewhere).

The temperature dependence of the dielectric constant is illustrated in Fig. 8. For all films broad transition peaks were observed that were attributed to different effects involving stress states and stoichiometry gradients.\(^{14}\) The most striking result, however, is the dramatic decrease in the transition temperatures of the films deposited on LSMO in comparison to the values obtained on Pt. While a \(T_C\) temperature of 440°C is obtained for PET5 on Pt, Fig. 8(b), it drops by more than 120°C for PET5 on LSMO. Figure 8(b) shows that PST5 behaves similarly, although slightly different values were obtained on Si and YSZ substrates. The values of \(T_C\) obtained on LSMO were found to be very similar to that of PLT10 on Pt. Furthermore, the nature of substrate does not affect the transition temperature of PLT10. Table I summarizes the \(T_C\) values obtained for the different films investigated.

The main factor reported in literature that can affect the transition temperature is stress which, for polycrystalline films, is mainly due to mismatch in the thermal expansion coefficients in the heterostructure.\(^{15,16}\) The question then arises as to why the transition temperature of PLT10 practically remains unchanged regardless of substrate. Furthermore, Er and Sm-doped PZT behave differently than PT insofar that the \(T_C\) temperatures of films on LSMO and Pt are very close to each other. This is exemplified in the case of PSZT in Fig. 8(c).

**D. X-ray photoelectron spectroscopy**

It appears that thermal stresses cannot be made responsible for the substantial shifts of the \(T_C\) temperatures of PT. In order to investigate diffusion processes between the underlying LSMO electrode and the PT layer, specimens prepared according to the procedures depicted in Sec. II were analyzed by XPS. It must be first pointed out that a detailed

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**TABLE I. Curie transition temperatures \(T_C\) and room temperature dielectric properties of the investigated thin-film heterostructure (data obtained at 1 kHz).**

<table>
<thead>
<tr>
<th>Heterostructure</th>
<th>(T_C) (°C)</th>
<th>(\varepsilon')</th>
<th>(\tan\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Pt/PET5/Pt</td>
<td>434</td>
<td>281</td>
<td>0.017</td>
</tr>
<tr>
<td>Si/Pt/PST5/Pt</td>
<td>404</td>
<td>382</td>
<td>0.027</td>
</tr>
<tr>
<td>Si/Pt/PLT10/Pt</td>
<td>328</td>
<td>797</td>
<td>0.049</td>
</tr>
<tr>
<td>Si/LSM0/PLT10/Pt</td>
<td>330</td>
<td>1059</td>
<td>0.42</td>
</tr>
<tr>
<td>Si/LSM0/PET5/Pt</td>
<td>316</td>
<td>574</td>
<td>0.17</td>
</tr>
<tr>
<td>YSZ/LSM0/PET5/Pt</td>
<td>316</td>
<td>183</td>
<td>0.10</td>
</tr>
<tr>
<td>YSZ/LSM0/PST5/Pt</td>
<td>305</td>
<td>184</td>
<td>1.3</td>
</tr>
</tbody>
</table>

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**FIG. 6.** Ferroelectric hysteresis loops of the PST5 (a) and PET5 (b) films deposited on the different substrates (indicated in the legend).

**FIG. 7.** Frequency-dependent dielectric properties of the PET5 (a) and PST5 (b) films deposited on the different substrates (indicated in the legend).
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analysis of peak shapes and peak energies is beyond the scope of this work, and that a qualitative analysis of the results is sufficient for the discussion below.

Although overlapping of peak energies complicates the interpretation of the results, Fig. 9 shows that there is strong evidence of the diffusion of lanthanum and manganese in the PET5 layer. The presence of lanthanum is uncontested, and the modification of the shape of the Pb 4p peaks by overlapping Mn 2p peaks [note the shoulder of the Mn 2p3/2 on Pb 4p3/2 visible in Fig. 9(b)] points to the presence of Mn at the PET5 surface. Stronger evidence of interdiffusion is obtained when LSMO is deposited on PET and analyzed. Figure 10 shows unambiguously that both Pb and Ti diffuse to the surface of LSMO.

IV. DISCUSSION AND CONCLUSIONS

The results depicted above show that the substrate material has a dramatic effect on the dielectric properties of lead titanate based films. Although in all cases the perovskite phase structure was obtained, its chemistry and necessarily its defect structure depend largely on the electrode material used. In the case of Pt, there is little interaction with the ferroelectric film, though some studies report the formation intermetallic template layers at early stages of film formation or disturbed interfacial layers, which were made responsible for the dimension effects (thickness dependence of the electrical properties) in lead-titanate based ferroelec-

FIG. 8. Temperature dependence of the dielectric constant for the PET5, PST5, and PLT10 thin films deposited on LSMO (a) and on Pt (b); (c) shows the results of PSZT on Pt and LSMO.

FIG. 9. (a) XPS peaks of La 3d for LSMO on Si and after deposition of one layer PET5; (b) Mn 3p XPS peaks of LSMO on Si and overlapping of Mn 3p with Pb 4p after deposition of one layer PET5 on LSMO. The inset shows the Pb 4p peak of PET5 on Pt.

FIG. 10. (a) XPS overviews comparing LSMO on Si and after deposition of one layer LSMO on top of PET5. The area outlined shows the Pb and Ti peaks not present in the spectrum of LSMO on Si; (b) peak details of Pb 4d and (c) peak details of Ti 2p.
tric thin films.\textsuperscript{18,19} The most pronounced effect on the chemistry of PbTiO$_3$ films, however, can be attributed to the LSMO electrode. The XPS results presented above are unambiguous in this respect. They clearly show ionic diffusion from LSMO towards the ferroelectric film and vice versa. From LSMO, La and Mn ions diffuse into the ferroelectric, whereas Pb and Ti ions diffuse from the ferroelectric into LSMO. It is expected that La$^{3+}$ substitutes Pb$^{2+}$ while Mn$^{3+}$ replaces Ti$^{4+}$. The substitution of Pb with La can be regarded as donor doping with the creation of cation vacancies following the reaction:\textsuperscript{20,21}

$$La^{3+} \rightarrow La_{ps}^{*} + xV_{pb}^{m} + yV_{ti}^{m*} \quad (2x + 4y = 1).$$  (1)

Mn is a small ion that can take divalent and trivalent oxidation states (a 4+ valence state is also possible but thermodynamically unstable). Substitution on Ti$^{4+}$ sites is compensated by the creation of oxygen vacancies and/or the annihilation of cation vacancies, following the reactions:\textsuperscript{20,21}

$$Mn_{2}O_{3} \rightarrow 2Mn_{ps}^{*} + 3O_{2} + V_{O}^{*},$$  (2)

$$MnO \rightarrow Mn_{Ti}^{m} + O_{2} + V_{O}^{*},$$  (3)

and/or

$$Mn^{3+} + xV_{pb}^{m} + yV_{ti}^{m*} \rightarrow Mn_{Ti}^{m} \quad (2x + 4y = 1),$$  (4)

$$Mn^{2+} + xV_{pb}^{m} + yV_{ti}^{m*} \rightarrow Mn_{Ti}^{m} \quad (2x + 4y = 2).$$  (5)

It is beyond the scope of this work to discuss the defect structure in LSMO/PbTiO$_3$ based heterostructures. It is nevertheless thought that fast diffusing species such as Pb$^{2+}$ and Ti$^{4+}$ might be responsible for a high defect concentration of the ferroelectric thin film.

It appears plausible to state that the changes of the dielectric properties are intimately related to changes in the stoichiometry of the ferroelectric film as a result of diffusion phenomena. That the $T_C$ of PLT10 is not affected by the substrate type suggests that La diffusion plays an important role in altering $T_C$ of Sm and Er doped PbTiO$_3$ deposited on LSMO. In the case of PLT10 the chemical driving potential for La diffusion is probably negligible.

The question then arises as to why the $T_C$ of Er and Sm doped PZT are not influenced by the type of substrate. Obviously ionic transport phenomena between LSMO and PZT do not occur or at least are of short range nature. An explanation could be found if it is supposed that a barrier layer forms between the LSMO and PZT films. Such a barrier layer may have a stoichiometry corresponding to the pyrochlore phase La$_2$Zr$_2$O$_7$. Although evidence of the existence of such layer is still to be found, it is quite known that both La and Zr are strong stabilizers of pyrochlore.\textsuperscript{22} The formation of an interfacial pyrochlore layer may have strong effects in impeding ionic transport in the heterostructures.

In conclusion, the present work shows that the use of LSMO as bottom electrode for lead titanate-based films affects strongly their chemistry and consequently their properties. The ferroelectric to paraelectric phase transformation temperature has been shown to be strongly reduced. XPS studies show that such effects are mainly due to ionic interdiffusion phenomena. Based on a comparative study of La doped lead-titanate thin films, it is assumed that the diffusion of La from the electrode to the ferroelectric (and that of Pb from the ferroelectric to the LSMO layer) is probably responsible for the reduction of the transition temperature.

ACKNOWLEDGMENTS

Thanks are due to Dr. K. Rätzke (Chair of Multicomponent Materials, Faculty of Engineering, Christian-Alberchts University of Kiel, Germany) for useful discussion. The financial support of the “Technologie-Stiftung Schleswig-Holstein” is gratefully acknowledged.