Microstructure and growth mode at early growth stage of laser-ablated epitaxial Pb(Zr_{0.52}Ti_{0.48})O_{3} films on a SrTiO_{3} substrate

W. C. Goh, a) S. Y. Xu, S. J. Wang, and C. K. Ong

Center for Superconducting and Magnetic Materials (CSMM), and Department of Physics,
Lower Kent Ridge Road, National University of Singapore, Singapore 119260

(Received 9 November 1999; accepted for publication 24 January 2001)

The surface morphology and microstructure of laser-ablated Pb(Zr_{0.52}Ti_{0.48})O_{3} (PZT) films on a (100) SrTiO_{3} (STO) substrate at early growth stage are characterized by means of atomic-force microscope, x-ray diffraction, and high-resolution transmission electron microscopy analysis. The (100) STO surface is found to be very favorable for epitaxial growth of (001) PZT films, which undergo a three-dimensional island growth mode. We observed a two-layer structure at the film thickness around 40–50 nm when small nuclei/grains merge into large grains. With further increase of film thickness, a column-like growth mode dominates the film crystalline structure, which results in an almost independent in-plain grain size of 100–150 nm with increasing film thickness and a limited film roughness. A very sharp interface between the PZT thin film and STO substrate is observed. The PZT film shows a perfect stacking lattice at a thickness of around 20 nm and above, indicating that the misalignment due to the interface stress and defects is healed after stacking about 50 ML of the film. These results have shed some light on the growth mechanism of epitaxial PZT film on YBCO or other bottom layers for microelectromechanical systems application. © 2001 American Institute of Physics. [DOI: 10.1063/1.1356426]

I. INTRODUCTION

Piezoelectric materials, in particular, lead–zirconate–titanate Pb(Zr_{x}Ti_{1-x})O_{3} (PZT), have shown very promising results for several applications such as nonvolatile memory elements, infrared sensors, surface acoustic wave devices, and actuators. As microelectromechanical systems (MEMS) start to receive more attention, the potential of PZT in micromotor applications becomes even more attractive. Researchers have been able to fabricate ultrasonic motors with PZT bulk materials. One such motor is the famous Sashida motor, which is ring shaped, using piezoelectric materials to generate a rippled surface on the metal attached to the piezoelectric material. This rippled surface, when in contact with a free rotating disk (held in place by a small force at the center axis), will move the disk through the frictional force between the two surfaces. Recently, micromotors using PZT films have been demonstrated, and several groups have been racing towards producing film-based motors with higher torque and higher power for practical applications.

Our research interest is to develop ultrasonic micromotors and sensors with piezoelectric films, and to integrate the devices with high-temperature superconducting (HTS) thin-film-based sensors into products of the current semiconductor processing industry. As an important step, we have fabricated high-quality thick multilayers of a (001)PZT/(001)YBCO/(100)YSZ epitaxial heterostructure on a (100)Si wafer by using the pulsed-laser deposition (PLD) technique, where YBCO (YBa_{2}Cu_{3}O_{7}−δ), a HTS material, is used as the bottom electrode, YSZ (yttria-stabilized zirconia) is used as both a diffusion buffer layer and a lattice-matching layer, and the PZT is as thick as 6 μm. As is well known, besides the PLD technique, several approaches such as sol–gel, rf sputtering, and the jet-mould system have been used to fabricate piezoelectric films. Compared to these methods, PLD has merits in excellent control of the stoichiometry of the film with complex components, a wide range of ambient reactive gas pressure, and flexibility of multilayer deposition. It is also relatively easy to obtain well-crystallized and oriented films by using PLD. As we have just mentioned, in our previous work, YBCO is chosen as the bottom electrode instead of a conventional metal layer. Lately, this issue has been extensively studied, and the results of which have clearly shown the advantages in structure compatibility, chemical stability, and fatigue-resisting property, by replacing metallic electrodes with conducting oxides like YBCO, LaNiO_{3}, and SrRuO_{3}. Here, both PZT and YBCO have a perovskite structure with a similar lattice constant in their a/b planes (a=3.81 Å and b=3.88 Å for YBCO, a=b=4.04 Å for PZT), and both require oxygen as the reactive gas during PLD process. We believe that the structural compatibility and similarity between them will not only improve the performance of the device made from the multilayers, but also make it possible to realize all-(perovskite)-oxide devices that utilize the merits of HTS, ferroelectric and, semiconducting properties.

In order to obtain high-quality PZT/YBCO thick (in this article, referring to the order of μm) films for MEMS application, it is essential to understand the correlation between the microstructure and piezoelectric property of the film. The final microstructures of the thick PZT film, in terms of crystalline structure, orientation, grain size, grain boundaries, second phases, impurities, defects, surface roughness, etc.,...
are to a certain level determined by the early stage of the film growth. In this article, we will report our investigations on the early growth stage of the epitaxial (001) Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ film on a (100) SrTiO$_3$ (STO) substrate. As there are no commercially available YBCO substrates, we choose STO as the substrate because it is also a perovskite material and has only a slight lattice mismatch ($a = 3.905$ Å) with those of (001) YBCO ($a = 3.81$ Å and $b = 3.88$ Å). The second reason is that the surface roughness of the YBCO film deposited using PLD, typically, 5–10 nm, does not fulfill our requirement for studying the initial growth of the PZT film. By depositing a PZT on STO substrate, which has an atomic-smooth surface, we will have a direct and clear view of the early growth stage of the PZT film on the lattice-matched substrate. Since STO and (001) YBCO have very similar lattice constants, we believe that the study will offer valuable clues on the growth mechanism of (001) PZT on top of the (001) YBCO thin-film surface in PZT/YBCO/YSZ/Si multilayers.

II. EXPERIMENTAL DETAILS

The PLD system employed in this experiment has been successfully applied to fabricate many high-quality epitaxial thin films. A KrF excimer laser (Lambda Physik, 248 nm wavelength, 30 ns pulse width) is used to ablate the PZT target. The sintered PZT ceramic targets have a stoichiometry of Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$. The target-to-substrate distance is 3.5 cm, and the incident angle of the laser with respect to the target surface is around 45$^\circ$.

Well-polished (100) STO single crystals with size of 10 mm×10 mm×0.5 mm are used as the substrates. The as-purchased STO substrates are cleaned in HF ($pH = 4.5$) aqueous solution for 1 min by ultrasonic vibration to remove the residual oxide layer on the surface and to smoothen the substrate surface. Then, the substrates are rinsed subsequently in deionized water, acetone, and ethanol with the ultrasonic cleaner. The substrates are kept in pure alcohol solution before transfer into the chamber for deposition. This is to avoid any contamination from the surrounding environment. Before each deposition, the substrate is mounted on the heater with a step, with its back against the heater surface. A little bit of silver paste is used at the two top corners of the substrate to secure it. Then, the chamber is immediately evacuated down to a vacuum pressure of around $10^{-5}$ mbar. A substrate temperature of 650°C was used for all the samples. Our previous studies have shown that a substrate temperature of higher than 600°C is preferred as it promotes the formation of the perovskite phase with better piezoelectric properties.

Ablation of the PZT layer is carried out at a laser fluence of 3.0 J/cm$^2$ and frequency of 5 Hz, under 0.11 mbar of ambient oxygen pressure. The parameters mentioned above are kept the same for all the samples, except for the deposition time. A series of samples with different deposition times, i.e., 1, 3, 6, 10, 20, 30, and 40 min, and therefore different thicknesses, are fabricated for this study. We have blocked a small corner of the sample with another substrate prior to deposition such that we can measure the film thickness by using a surface step profiler. After the deposition, the samples are annealed under 1 bar of oxygen for 30 min at 600°C before they are naturally cooled down to room temperature.

The as-deposited films are characterized right after the deposition process. The crystalline phases and orientation of the films are characterized by using x-ray diffraction (XRD) $\theta$–2$\theta$ and $\theta$ scans (rocking curve scan). The morphology of the films is studied by using an atomic-force microscope (AFM, Nanoscope IIIa) operating under tapping mode. A high-resolution transmission electron microscopy (HRTEM, Philips CM 300) is applied to study the microstructure and interface between the PZT film and STO substrate. The cross-section specimens for the HRTEM studies are prepared using the standard preparation method including polishing, mechanical dimpling, and ion-beam milling.

III. RESULTS AND DISCUSSION

Table I lists some of the measured results. The films are well crystallized and oriented, as revealed by XRD analysis. All the PZT films are oriented with their $c$ axis perpendicular to the substrate surface. Figure 1 shows the XRD $\theta$–2$\theta$ scan patterns of the PZT film deposited for 20 min, where only high and sharp (001) and (002) peaks of PZT and peaks of the STO substrate are observed. The two peaks marked as “S” are calibrated to be from the STO substrate. Careful

<table>
<thead>
<tr>
<th>Deposition Time (min)</th>
<th>Thickness by Step Profiler (nm)</th>
<th>Thickness by HRTEM (nm)</th>
<th>FWHM of PZT (002) rocking curve (°)</th>
<th>In-plane average grain size (nm)</th>
<th>AFM root mean square roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19</td>
<td>17</td>
<td>0.64</td>
<td>1.3</td>
<td>1(1)</td>
</tr>
<tr>
<td>3</td>
<td>58</td>
<td>52</td>
<td>1.48</td>
<td>30</td>
<td>1(1)</td>
</tr>
<tr>
<td>6</td>
<td>116</td>
<td>104</td>
<td>0.59</td>
<td>100</td>
<td>5.6(2)</td>
</tr>
<tr>
<td>10</td>
<td>193</td>
<td>173</td>
<td>0.69</td>
<td>140</td>
<td>7.7</td>
</tr>
<tr>
<td>20</td>
<td>385</td>
<td>347</td>
<td>1.22</td>
<td>160</td>
<td>8.0</td>
</tr>
<tr>
<td>30</td>
<td>578</td>
<td>520</td>
<td>0.47</td>
<td>150</td>
<td>9.2</td>
</tr>
<tr>
<td>40</td>
<td>770</td>
<td>693</td>
<td>1.30</td>
<td>170</td>
<td>11.9</td>
</tr>
</tbody>
</table>

(1) Underlying small grains layer.
(2) Top larger grains layer.

FIG. 1. XRD $\theta$–2$\theta$ scan of the PZT film deposited on a SrTiO$_3$ (100) substrate for 20 min.
step scans on the (001) peak of the PZT films revealed that there is a small change in the lattice constant $c$ along the $c$ axis, i.e., $c$ increases by 0.6% as the film thickness increases from 18 to 580 nm (Fig. 2). In addition to the factor of measurement error, this change in $c$ may be partially attributed to the relief of the stress generated at the PZT/STO interface when the films get thicker. The full width half maximum (FWHM) in the rocking curve of the PZT (002) peak (Table I and Fig. 2) shows varying values ranging from 0.46° to 1.48° without any particular trend. This might be caused by the uncertain surface condition of the STO substrate, e.g., a different miscut degree and different defect density. This result implies that the thick PZT film (in μm) is not necessarily associated with poor crystalline orientation. Indeed, in our previous studies, FWHM values of 0.50° and 0.60° were obtained for the (001) PZT rocking curve in a 2-μm-thick PZT film on STO and a 6-μm-thick PZT film on Si, respectively.\(^\text{11}\) The insensitivity of film crystalline orientation to the film thickness observed here is definitely an advantage towards the goal of thick PZT films for MEMS applications. The underlying mechanism will be discussed later in the article.

The morphology analysis reveals some important clues of the growth mechanism of PZT on STO. Figure 3 shows the typical AFM micrographs of films with different thicknesses as well as the STO substrate after the cleaning process mentioned above. Figure 3(a) shows the terrace steps on the STO surface with a height of one lattice layer (~0.4 nm), indicating a miscut of ~0.2°. Figure 3(b) is the morphology obtained after the deposition of the PZT film for 1 min (~18 nm in thickness) on the STO substrate. At this stage, the film has small nuclei/grains that grow uniformly across the substrate. However, there are voids in the film, which means the substrate surface has not been fully covered yet. When the deposition time is increased to 3 min [Fig. 3(c), film thickness ~55 nm], we can see that a layer of large grains appears on top of the small grain layer. The lower layer has an average grain size of 25–30 nm, and it has fully covered the substrate surface. The upper layer, on the other hand, has an average grain size of 100–120 nm, three times bigger than that of the former. However, at this stage, the upper layer covers only about 30%–40% of the film area. The cross-section analysis from the AFM micrograph (Fig. 4) shows that the difference in between the surface of the large grains and that of the bottom small grains is ~15 nm. In other words, the large grains begin to form at a film thickness of around 40 nm, nearly 100 ML of the (001) PZT film.

As the deposition time is increased to 6 min [Fig. 3(d), thickness ~110 nm], the film structure appears uniform all over the substrate surface, and most of the grains are separated with clearly defined grain boundaries. When the deposition time is further increased to 20 min or above [Figs. 3(f), 3(g), and 3(h)], some large grains of submicron or micron size appear. Some of them may be caused from the coalescence and merging of the smaller grains, others may be caused by second-phase particles, precipitates, and droplets—a typical feature observed in laser-ablated thin films due to the well-known “splashing” effect. This trend results in the formation of irregular-shaped grains and also causes an increase in the film roughness. But, surprisingly, if these large particles are not counted, the average in plane grain size of the “main body” of the film does not obviously increase with the increase of the film thickness (Table I and Fig. 5).
From the above results, we suggest that the epitaxial (001) PZT films grown on a lattice-matched (100) STO substrate has undergone a three-dimensional (3D) island growth mode. In the early growth stage, nuclei are uniformly distributed on the substrate surface. At the thickness of around 45 ML of the film (~18 nm), nuclei coalesced but the substrate surface is still not fully filled. The critical nucleus size of ~25–30 nm and a nucleus density of ~1.5 × 10¹¹/cm² are observed [Figs. 3(b) and 3(c)]. At about 100 ML (~40 nm) of the film, the substrate surface is completely covered. As some of the grains reach the critical size of nucleation, it will start to grow in size and incorporate the surrounding grains, which are smaller, leaving two layers of the film exposed. With the increase of film thickness, the film is occupied with all large grains with irregular shapes and nonuniform sizes as they are coalesced and merged. When the film thickness further increased, the shapes and sizes of the grains became more irregular, meanwhile the roughness of the film increased. However, with the increase of film thickness, the average grain size is kept at ~100–150 nm. This is a typical column-like structure that is often observed in laser-ablated epitaxial thin films with complex components. For example, a c-axis YBCO thin film prepared at 700–750 °C usually shows a column structure with its in-plane grain dimension of 0.2–0.4 μm.²⁷ But, in the film with simple components, the apparent grain size may keep on increasing with the increase of film thickness.²⁸

It is expected that this trend of column-structure growth still dominates in thicker PZT films, as long as the deposition conditions are not changed. Such a columnar growth structure has been also observed by some other researchers.²⁹ As mentioned above, (001) of YBCO, (001) of PZT, and (100) of STO have only a small lattice mismatch. Hence, it is reasonable to assume that what is observed in the (001)PZT/(100)STO structure may be also true, or at least partially true, for the case of the (001)PZT/(001)YBCO multilayer. Indeed, we did observe an average in-plane grain size of 120–150 nm is observed in a 6-μm-thick (001) PZT film on (001)YBCO/(100)YSZ/(100)Si prepared by PLD.¹¹ To account for this phenomenon, the substrate temperature and impinging energy of the species in the laser-generated plume are two main factors to be considered,¹⁵,¹⁶,²¹ which determine the diffusivity of the adatoms on the film surface. In addition, the structure and components of the grain boundaries in the PZT film may also play an important role, for somehow they restrict the merging effect of neighboring grains, thus limiting the final in-plane grain size.

Figure 6 shows the schematic diagram of the film growth
structure to illustrate why the orientation of PZT films is insensitive to the film thickness. Column growth maintains the crystalline orientation and quality in the process of thick PZT films and enables one to obtain a uniform performance of the film under an external electric field. The column structure seems to be advantageous in limiting the surface roughness. We have observed from AFM images that between two different points on the top surface of the grain the absolute difference in height was less than 1/3 of the in-plane horizontal grain size. For the grain size of 100–150 nm of the PZT films, it means that the root-mean roughness is limited to less than 50 nm. For a 10 μm PZT film, this limitation equals only 0.5% of the film thickness and is, therefore, acceptable. These two merits of the column growth mode, namely, fixed film orientation and limited surface roughness, are all very helpful for MEMS applications, e.g., PZT-film-based micromotor.

Next, we further investigate the microstructure of the PZT films and the interface of PZT/STO by using HRTEM. Figure 7 is a HRTEM cross-section view of the PZT film deposited on a STO substrate for 3 min, showing a uniform thickness of 52–55 nm. Comparing the thickness measured from the HRTEM cross-section view to those measured with the step profiler, we find that the difference is around 10%. The final values of the film thickness used in the above discussion are the average of the two sets of measured results. Using high magnification, we can clearly see the PZT/STO interface, as shown in Fig. 8. Since the lattice mismatch between PZT and STO is very small, the PZT film is commensurately epitaxial on the STO substrate. The crystalline correlations in Fig. 8 are (001)PZT||(100)STO and [110]PZT||(011)STO. The interface is clear and sharp, and the lattice distortions occur only in a region of 1–2 nm around the interface, marked as “A” in the micrograph. A few nm away from the interface, there are also some local misalignments of the PZT lattice, marked as “B” in the micrograph. Defects in zone “A” are obviously mainly caused by the defects on the STO substrate, while the defects in zone “B” may be attributed to the impurity and stacking faults in the film. About 20 nm away from the interface and further, the crystalline structure of the PZT film appears almost perfect. In general, we may state that the misalignment due to the interface stress and substrate surface defects is healed with stacking about 50 ML of the PZT film. Even at the substrate surface with a serious defect, e.g., a big step, the PZT film can still stack perfectly after a few nm of misalignment. Figure 9 shows such a case. The HRTEM analysis shows that the STO substrate is very favorable for the epitaxial growth of the PZT film.

IV. CONCLUSION

In this article, the early growth stage of an epitaxial PZT thin film on a STO substrate is studied in terms of surface morphology, crystalline orientation, microstructure, and film–substrate interface. We have obtained several valuable clues of the growth mechanism. The (100) STO surface is found very favorable for the epitaxial stacking of the (001) PZT lattice. The epitaxial (001) PZT film on (100) STO appears to undergo a 3D island growth mode. The nuclei of the PZT film, with a size around 25–30 nm and a density of the order of 10¹¹/cm², are found uniformly distributed on the STO substrate surface. However, the substrate surface is not...
fully filled when initial 40–50 ML have been stacked. We have observed a two-layer structure in the early stage of the film growth, at a film thickness of around 40–50 nm or around 100 ML, where small nuclei/grains (25–30 nm in diameter) are merged into larger grains (100–120 nm in diameter). With a further increase of the film thickness, the films show a dominant column-like growth mode and crystalline structure in all samples thicker than 115 nm, keeping an average grain size ranging from 100 to 150 nm. However, when the films become thicker, the shapes and sizes of the grains become more irregular, meanwhile the roughness of the films increases. We suggest that this trend of column structure growth still dominates in even thicker PZT film, provided that the deposition conditions are not changed. The column growth of the PZT film is believed to be advantageous for MEMS application as it keeps the crystalline orientation and preserves the quality in processing thick PZT film as well as limiting the overall surface roughness of the film.

Our HRTEM observation of the samples reveals a very sharp interface between the PZT thin film and STO substrate, where the (001) PZT film is nearly commensurately epitaxial on the (100) STO substrate. Distortions of the lattices occur only in a region of 1–2 nm around the interface, even at the substrate surface with a serious defect like steps. Regions with local lattice misalignment are also observed in the PZT film several to 10 nm away from the PZT/STO interface. The PZT film shows a perfect stacking lattice at a thickness of 20 nm and above, indicating that the misalignment due to the interface stress and substrate defects is healed with stacking about 50 monolayers of the PZT film.

These results will shed some light on the growth mechanism of epitaxial PZT film on YBCO in our PZT/YBCO/YSZ/Si multilayer for micromotor/MEMS application.

ACKNOWLEDGMENT

This project is financially supported by the National University of Singapore.