Characteristics of Ba(Mg$_{1/3}$Ta$_{2/3}$)$_3$O$_7$ thin films prepared by pulsed laser deposition process and their effect on the growth of Pb(Zr$_{1-x}$Ti$_x$)$_3$O$_7$ thin films

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The growth behavior of Ba(Mg$_{1/3}$Ta$_{2/3}$)$_3$O$_7$ (BMT) thin films on bare or Pt-coated silicon substrates and their buffering effect on the subsequently deposited Pb(Zr,Ti)O$_3$ (PZT) films were systematically examined. The preferred orientation of BMT layer varies pronouncedly with the deposition parameters. It is (200) textured when deposited under high substrate temperature (400 °C) or large laser fluence (3 J/cm$^2$). The BMT layer not only suppresses the film-to-substrate interdiffusion but also enhances the Pb(Zr$_{1-x}$Ti$_x$)$_3$O$_7$ (PZT) nucleation kinetics. The PZT films prepared on BMT layer by metal-organic-decomposition (MOD) process begin to crystallize at a substrate temperature as low as 400 °C, which is lower than the reported heat treatment temperature for preparing PZT films via MOD process. However, postannealing at 550 °C is required to fully crystallize the PZT films. The PZT/BMT/Pt thin films show high dielectric constant ($\varepsilon_r$) of 400–425, low leakage current density ($J_{leak}$ < 2 × 10$^{-7}$ A/cm$^2$), and good ferroelectric properties ($P_c$ = 15 μC/cm$^2$, $E_C$ = 157 kV/cm), while the PZT/BMT/Si thin films exhibit a large optical refractive index ($n_{PZT/BMT/Si}$) = 2.4. © 2004 American Institute of Physics.

I. INTRODUCTION

Pb(Zr$_{1-x}$Ti$_x$)$_3$O$_7$ (PZT) thin films have alluring applications such as nonvolatile ferroelectric random access memory$^{1-3}$ and optical waveguide devices$^{4,5}$ owing to their splendid ferroelectric/piezoelectric properties. The direct growth of PZT thin films on bare silicon substrates is intricate because PZT interacts with substrate materials, degrading the sought after ferroelectric properties. A buffer layer$^{6-12}$ has been incorporated to suppress the PZT-to-Si interdiffusion and thus enhance the ferroelectric behavior of the PZT thin films. The synthesizing temperature for PZT films (>550 °C) is significantly lower than their ferroelectric counterparts, such as, SrBi$_2$Ta$_2$O$_9$. However, it is still much higher than processing temperature employed in Si devices. This is a hurdle for direct integration of PZT films in integrated circuitry.

In this paper, we report the use of a buffer layer Ba(Mg$_{1/3}$Ta$_{2/3}$)$_3$O$_7$ (BMT) to simultaneously suppress the PZT-to-Si interdiffusion and enhance the nucleation of PZT crystalline phase for lowering the growth temperature of PZT thin films. The growth behavior of BMT buffer is systematically investigated and the advantage of using BMT as buffer layer for PZT is demonstrated.

II. EXPERIMENT

The BMT target materials were prepared by conventional mixed oxide method, in which the BMT powders were pelletized and then sintered at 1500 °C for 4 h. The BMT thin films were synthesized by a pulsed laser deposition (PLD) process. A KrF excimer laser (248 nm) with 2–3 J/cm$^2$ fluence was used with a target to substrate distance of 7 cm. The BMT buffer layer was grown in situ on bare or Pt-coated Si substrates at 300–400 °C for 30 s to 30 min with the oxygen pressure maintained at 0.1 mbar. PZT thin films were subsequently deposited on BMT-buffered Si [or Pt(Si)] by metallo-organic decomposition (MOD) method. Lead 2-ethylhexanoate [Pb(C$_7$H$_{15}$COO)$_2$], zirconium 2-ethylhexanoate [Zr(C$_7$H$_{15}$COO)$_4$], and titanium di-ethoxy-di-2-ethylhexanoate [Ti(OOC$_2$H$_4$)$_2$(C$_7$H$_{15}$COO)$_2$] were used as precursors for preparing the 0.3M Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ solutions. The PZT thin films were spin coated onto BMT-buffered substrates, dried at 140 °C for 10 min, and then pyrolyzed at 400 °C for 30 min. The process was repeated till the desired thickness of 300 nm was achieved. The amorphous PZT films thus obtained were then annealed between 400 and 700 °C for 1 h.

The x-ray diffractometer (XRD, Rigaku DMX) was used for examining the phase constituents as well as crystallinity, while the scanning electron microscopy (SEM, Jeol, JSM 6300) was used for examining surface morphology for these thin films. Dielectric properties of the PZT films were measured by Impedance Tester (Agilent, H. P. 4192) and ferroelectric properties of the films were measured by a hysteresis loop tracer (Aixacct, TF Analyzer 2000). Finally, optical properties of the PZT films were measured by prism coupling method (Metricon, Model 2010).
III. RESULTS AND DISCUSSION

Unlike the PZT thin films, BMT materials do not interact with Si substrate and form perovskite easily on these substrates by PLD process. Figure 1(a) shows that crystalline BMT films can be obtained for a substrate temperature as low as 300 °C ($P_{O_2}$=0.1 mbar). The preferred orientation of the BMT films varies markedly with the substrate temperature, viz., the films are (110)-preferentially oriented when deposited at 300 °C and are (200)-preferentially oriented when grown at 400 °C. The texture characteristics of the films also vary with deposition pressure and laser fluence. The relative fraction of (200)-oriented grains increases as deposition pressure decreases [Fig. 1(b)] or as the laser fluence increases [Fig. 1(c)]. For the BMT films deposited at 300 °C, the variation of relative intensities (200)/(100) with two deposition parameters [Fig. 1(d)] reveals that the (200)-textured BMT films can either be obtained by growing the films at substrate temperature high enough (400 °C) or by using sufficiently large laser fluence (3 J/cm²). A change in deposition pressure does not alter the texture characteristics significantly, although a low deposition pressure reduces the collision frequency of species-to-gas molecules and results in higher kinetic energy for laser ejected species.

BMT thin films, which form perovskite phase directly on Si substrates, can not only suppress the interdiffusion between PZT and Si materials, but also enhance the nucleation of PZT crystalline phase. Figure 2 shows that, for the PZT films deposited on BMT-buffered Si substrates by MOD process, the perovskite phase was already present when the films
were postannealed at a temperature as low as 400 °C (1 h). This temperature is lower than the onset temperature for forming perovskite PZT thin films by MOD process reported in the literature11–14 (listed in Table I). However, postannealing at higher temperature (550 °C, 1 h) is necessary to fully crystallize the PZT films. It should be noted that the underlying BMT buffer layers, 300 nm and (002)-preferredly oriented, were deposited in situ at 400 °C (0.1 mbar) by PLD process with 2 J/cm² laser fluence. The broadening of (200) diffraction peak in Fig. 2 for PZT/BMT/Si thin films is due to the slight difference in PZT and BMT lattice parameters, rather than the peak splitting due to tetragonality of the PZT films.

Moreover, Fig. 2 indicates that the PZT films experiencing 700 °C (1 h) postannealing process are still of pure perovskite phase. This implies that the PZT films deposited on BMT buffer layer not only start to crystallize at lower postannealing temperature, but also can withstand higher heat-treating temperature. SEM micrograph in Fig. 3(a) reveals that 550 °C postannealed PZT films contain very fine grains, about tens of nanometers while Fig. 3(b) shows that the grains grow moderately to about 100 nm when postannealed at 700 °C (1 h). The contours observed in this figure are the groovings resulted from grain growth rather than the micro-cracks, as illustrated by the inset of Fig. 3(b). Restated, high temperature posttreatment process only results in grain growth. There is no secondary phase induced.

Advantages of BMT buffer layer on the growth of PZT films are reinforced by the improvements on the optical properties of the films. The prism coupling measurements (not shown) indicate that the refractive index measured at 632.8 nm is around \( n \)\(_{\text{PZT/BMT/Si}} = 2.4 \) for PZT films grown on BMT-buffered (400 nm) Si-substrates and is only \( n \)\(_{\text{PZT/BMT/Si}} = 2.0 \) for those deposited on Si substrates directly without BMT buffer layer. As there is an intimate correlation between refractive index of materials and crystallization of films, such a result indicates that PZT/Si thin films contain a large proportion of lower index materials, presumably the amorphous PZT residing in PZT-to-Si interface region or between the PZT grains. Utilization of BMT as buffer layer strikingly enhances the crystallization kinetics for PZT thin films such that the presence of residual amorphous PZT phase is pronouncedly suppressed, which leads to higher optical refractive index for PZT/BMT/Si thin films.

For the purpose of evaluating the electrical properties of these films, synthesis of the films on platinum-coated Si substrates, Pt(Si), is necessary. Fortunately, BMT thin films can also form perovskite phase easily on Pt(Si) substrates and enhance the crystallization kinetics of subsequently deposited PZT films. Also, high substrate temperature or low oxygen pressure favors the formation of (200)-oriented BMT grains (not shown), and the texture characteristics of BMT films vary manifestly with the oxygen pressure than with the substrate temperature. Subsequently deposited PZT films inherit the texture characteristics of the BMT buffer layer. Figure 4 shows that either randomly oriented or (200)-textured PZT films can be obtained by controlling the texture characteristics of the BMT buffer layer. SEM micrographs in Figs. 5(a) and 5(b) respectively, indicate that both the BMT (~300 nm) and PZT films (~300 nm) are very dense, containing very fine grains (~<100 nm). Cross-sectional micrograph shown in Fig. 5(b) reveals once again that the contours observed for PZT films are groovings resulted from grain growth rather than microcracks.

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**TABLE I. The onset temperature for the formation of crystalline PZT thin film prepared by MOD process.**

<table>
<thead>
<tr>
<th>Thin films</th>
<th>( T_o ) (°C)</th>
<th>Buffer layer</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>PZT</td>
<td>530</td>
<td>LaNiO(_3)</td>
<td>11</td>
</tr>
<tr>
<td>PZT</td>
<td>500</td>
<td>SrRuO(_3)</td>
<td>12</td>
</tr>
<tr>
<td>PZT</td>
<td>600</td>
<td>–</td>
<td>13</td>
</tr>
<tr>
<td>PZT</td>
<td>600</td>
<td>–</td>
<td>14</td>
</tr>
</tbody>
</table>

\( T_o \): annealing temperature for onset for crystallization of PZT amorphous thin films.
To extract the dielectric properties of BMT films from the metal-insulator-metal structured PZT/BMT/Pt(Si) thin films, BMT films of different thicknesses (30–300 nm) were first deposited on Pt(Si) for 3–30 min, followed by MOD deposition of PZT films (300 nm). XRD patterns shown in Fig. 6(a) indicate that these BMT films are of randomly oriented perovskite phase and so are the subsequently deposited PZT films (not shown). The total dielectric constant \( (\varepsilon_r) \) for PZT/BMT/Pt(Si) thin films decreases with the thickness of BMT thin films, as shown in Fig. 6(b) (open squares). The dielectric properties of PZT and BMT layers can be extracted from these results by assuming that the total capacitances of the PZT/BMT/Pt(Si) thin films is the series combination of the capacitance of PZT and BMT layers. The dielectric constant of PZT layer thus calculated is \( (\varepsilon_r)_{PZT} = 400–425 \), whereas that of BMT layer increases with the thickness of the films \( [(\varepsilon_r)_{BMT} = 7–25, \text{solid circles in Fig. 6(b)}]. \)

Variation of \( (\varepsilon_r)_{BMT} \) with the film thickness is unexpected. Smaller dielectric constant for thin BMT films, i.e., \( (\varepsilon_r)_{BMT} = 7 \) for 30 nm BMT, infers that the first few layers of BMT films are amorphous, whereas large dielectric constant for thick BMT films, viz., \( (\varepsilon_r) = 25 \) for 300 nm BMT thin films, indicates that the crystalline phase appears when BMT films are thick enough. Detailed analysis on XRD patterns in Fig. 6(a) indicates that, for 30 nm BMT films, the peak intensity for BMT phase is very small and is accompanied by noisy background. These results imply that there exists some portion of noncrystalline phase when the BMT films are too thin, which is in accord with the dielectric measurements. The dielectric constant of PZT thin films measured is close to literature value, whereas the dielectric constant of BMT thin films is the same as that of bulk ceramic materials.

The PZT/BMT/Pt(Si) thin films grown on thick BMT buffer layer (300 nm) shows only paraelectric characteristics, as most of the external field was applied onto BMT layer due to its low \( \varepsilon_r \) value. Thinner BMT films are needed in order to improve the overall \( P-E \) characteristics of the PZT/BMT/Pt(Si) films. Figure 7(a) reveals that PZT/BMT(5 nm)/Pt(Si) films grown on 30 s BMT buffer layer (open diamonds) possess much better leakage properties than the PZT/Pt(Si) thin films grown on Pt(Si) directly (solid squares). However, these films still show large leakage current density in high voltage region. It requires at least 10 nm (60 s) BMT buffer layer to completely suppress the leakage behavior for the PZT films (open squares) and thus obtained PZT/BMT(60 s)/Pt(Si) thin films possess good \( P-E \) properties \( [P=15 \mu C/cm^2 \text{ and } E_c=157 kV/cm, \text{Fig. 7(b)}]. \)

To understand the sources leading to large leakage current for the PZT/BMT/Pt(Si) thin films, the microstructure of the thin BMT films (60 s, 10 nm) was examined. Figure 7(c) reveals that there exists large proportion of micropores whenever the BMT films are too thin (<10 nm). Although the porous BMT films can still promote the formation of PZT films, it is believed that, in the first stage of postannealing process, only the PZT materials sitting on top of BMT grains crystallize (primary crystals), whereas the PZT materials deposited on top of pores remain amorphous, which is schematically illustrated in Fig. 8(a). The residual amorphous
PZT crystallizes in the latter stage of postannealing process by lateral growth of the primary crystals [Fig. 8(b)], designated as secondary crystals. When the BMT buffer layer is too thin, e.g., 5 nm for 30 s deposited films, the fraction of primary PZT crystals is too less and residual amorphous may remain in grain boundary of secondary crystals, resulting in possible leakage path under large applied field.

IV. CONCLUSION

BMT perovskite thin films can be obtained for a wide range of deposition parameters in pulsed laser deposition process irrespective of substrates. The preferred orientation of BMT layer varies with deposition parameters and the subsequently deposited PZT films inherit the texture characteristics of the BMT buffer layer. The PZT films prepared by MOD process start to crystallize at a substrate temperature lower than the heat treatment temperature reported. PZT films grown on BMT/Si substrates possess significantly larger optical refractive index than those deposited without BMT buffer layer ($n_{\text{PZT/BMT/Si}} = 2.4$, $n_{\text{PZT/Si}} = 2.0$). The PZT thin films deposited on BMT/Pt(Si) substrates possess large dielectric properties, ($\varepsilon_r = 400–425$, low leakage current density ($J_e < 2 \times 10^{-7} \text{ A/cm}^2$), and good ferroelectric properties ($P_r = 15 \text{ \mu C/cm}^2$, $E_{c} = 157 \text{ kV/cm}$).