Preparation of PZT thin films on YBCO electrodes by KrF excimer laser ablation technique

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Abstract

Pb(Zr,Ti1-x)O3 (PZT) films have excellent ferroelectric, optical, piezoelectric, and pyroelectric properties. We prepared PZT thin films by the excimer laser ablation technique. A pulsed KrF excimer laser (Lambda Physik LPX305icc, pulse duration of 25 ns, λ = 248 nm, 850 mJ Max.) was used to ablate the bulk targets. We investigated the influence of bottom electrode materials on the characteristics of the PZT thin films prepared on Pt and YBCO underlayers. The X-ray diffraction (XRD) patterns showed that the PZT films prepared with a laser fluence of 2 J cm⁻² on YBCO/MgO(100) substrate at a wide temperature range of 550–680 °C have a perovskite (001) structure. At the same laser fluence, the PZT films prepared on Pt/MgO(100) substrate have a perovskite (001) structure only at 650 °C. The polarization–electric field (P–E) characteristics and fatigue properties of PZT thin films were measured by the Sawyer–Tower circuit. The remnant polarization and coercive field have been found to be $P_r = 15 \mu C cm^{-2}$, $30 \mu C cm^{-2}$ and $E_c = 200 kV cm^{-1}$, 100 kV cm⁻¹ for Au/PZT/Pt/MgO and Au/PZT/YBCO/MgO correspondingly. The remnant polarization of Au/PZT/YBCO/MgO thin film was reduced to one-half after about $10^8$ cycles of switching.

Keywords: KrF; Laser ablation; PZT thin films; YBCO electrodes

1. Introduction

Ferroelectric thin films offer a wide variety of applications such as non-volatile random access memories, surface acoustic wave (SAW) devices [1], pyroelectric detectors [2] and piezoelectric vibrators [3]. It is also pointed out that the superconducting electrode may be a better oxide electrode candidate for ferroelectric memory devices than the traditional Pt metal electrode. Recently, the high-temperature superconducting (HTSC)/ferroelectric hybrid structures have been of great interest in the fabrication of the superconducting field-effect transistor [4]. Specifically, Pb(Zr,Ti1-x)O3 (PZT) ferroelectric thin film has drawn much attention, because of the high dielectric constant and remnant polarization.

In this paper, PZT ferroelectric thin films were prepared using the excimer laser ablation technique [5]. We investigated the correlations between characteristics of PZT thin films and type of bottom electrode material:

Pt and YBCO. YBCO template layer provides a PZT capacitive structure with a higher remnant polarization, lower coercive field and higher stability against fatigue comparing with a Pt conducting underlayer.

2. Experimental

Fig. 1 shows a schematic of a KrF excimer laser deposition system. A KrF excimer laser (Lambda Physik LPX 305icc: λ = 248 nm, pulse duration of 25 ns, 850 mJ max.) was used to ablate a target in the deposition chamber (Ø 300 mm, stainless steel). We used a stochiometric bulk target of PbZr0.52Ti0.48O3, YBa2Cu3O7-x and Pt. The laser beam was irradiated on the small area (2 x 5 mm²) of the target at an incident angle of 45°. The target was rotated at 12 r.p.m. to avoid a surface texturing. A substrate was placed in front of the target. The distance from PZT and Pt targets to substrate was 40 mm, and that of the YBCO target was 50 mm. The substrate was heated by an infra-red lamp. After the chamber was evacuated to a base
pressure ($1 \times 10^{-5}$ Torr), using both rotary and turbo molecular pumps, oxygen gas was allowed into the chamber. First of all, the Pt or YBCO bottom electrodes were prepared on MgO(100) substrate, and then PZT thin films were deposited on these bottom electrodes. A Pt bottom electrode was deposited at 600 °C and with a laser fluence of 4 $\text{J/cm}^2$ [6]. The YBCO bottom electrode was deposited at 710 °C, with an oxygen pressure of 200 mTorr and a laser fluence of 2 $\text{J/cm}^2$ [7]. PZT thin films were prepared at 550-680 °C. These conditions are summarized in Table 1. After the deposition of PZT films, each heterostructure was annealed in an oxygen pressure of 400 mTorr for 15 min at the same temperature as PZT deposition condition. The crystalline structure and ferroelectric properties of PZT thin films have been studied to find a correlation between the PZT thin film performance and the bottom electrode material.

3. Results and discussion

3.1. Crystallization of PZT thin films

First of all, we investigated crystallization of PZT thin films on each bottom electrode. The crystalline structure was studied using X-ray diffraction (XRD) measurement. Fig. 2 shows the XRD spectra of PZT films prepared on the Pt/MgO substrate at substrate temperatures from 630 to 680 °C. In particular, the PZT/Pt/MgO thin film that was prepared at 650 °C has a remarkable perovskite (001) crystalline structure. This result indicates that 650 °C is the optimal substrate temperature for growing PZT(001)/Pt/MgO films, whereas the range of substrate temperature for perovskite (001) structure is very narrow.

Fig. 3 shows the XRD spectra of PZT/YBCO/MgO thin films. PZT films were prepared at substrate temperatures of 550-680 °C. The perovskite (001) structure is clearly seen for all these substrate temperatures. The range of substrate temperatures for the perovskite (001)
Table 1
Deposition condition for a KrF excimer laser deposition system

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Pt (99.99%)</th>
<th>YBCO</th>
<th>PZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy density (J cm⁻²)</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Repetition rate (Hz)</td>
<td>10</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Target</td>
<td>Pt</td>
<td>YBa₂Cu₃O₇₋ₓ</td>
<td>Pb₅(Zr₀.₅₂Ti₀.₄₈)O₃</td>
</tr>
<tr>
<td>Ambient gas</td>
<td>O₂</td>
<td>O₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Total pressure (mTorr)</td>
<td>10²</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>Substrate</td>
<td>MgO(100)</td>
<td>MgO(100)</td>
<td>Pt/MgO</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>600</td>
<td>710</td>
<td>550–680</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>60</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Film thickness (nm)</td>
<td>200</td>
<td>200</td>
<td>400</td>
</tr>
</tbody>
</table>

KrF excimer laser: Lambda Physik LPX305icc, λ = 248 nm, pulse duration 15 ns, 850 mJ max.

Structure is much wider than in the case of the PZT film prepared on the Pt bottom electrode. From these results, we infer that the YBCO bottom electrode is a good template layer for the crystallization of PZT(001) thin films.

3.2. Electrical property of PZT thin films

Next, we measured the electrical property of Au/PZT/Pt/MgO and Au/PZT/YBCO/MgO thin films. Gold top electrodes (Ø=200 µm) were prepared by thermal evaporation at room temperature.

Fig. 4 shows the polarization–electric field (P–E) hysteresis loops. These loops were measured by a Sawyer–Tower circuit at a frequency of 1 kHz. Fig. 4(a) shows the hysteresis loop of a Au/PZT/Pt/MgO thin film prepared at 650 °C. The remnant polarization was 15 µC cm⁻². The value of the coercive field E_c was about 200 kV cm⁻¹. Fig. 4(b) shows the hysteresis loop of Au/PZT/YBCO/MgO. The remnant polarization was about 30 µC cm⁻². The value of the coercive field was about 100 kV cm⁻¹. The Au/PZT/YBCO/MgO thin film has a much better electrical performance than the Au/PZT/Pt/MgO thin film. The results of Figs. 3 and 4 suggest that YBCO is more suitable for use as a bottom electrode of PZT thin films than Pt. Better ferroelectric properties of PZT film on the YBCO result from the higher crystallization of the YBCO template layer.

Next, we investigated the fatigue characteristic of PZT thin films. The fatigue characteristic is important for the application of PZT thin films.

We measured the remnant polarization by a Sawyer–Tower circuit at a frequency of 50 kHz.

Fig. 5(a) shows the fatigue characteristic of Au/PZT/Pt/MgO thin film. Within 10⁷ times of switching, the remnant polarization 2P_r decreased from 20 µC cm⁻² to 6 µC cm⁻². Thus, a rapid decrease in the rate of P_r indicates that PZT crystallization is not as good and is probably caused by using a polycrystalline Pt bottom electrode. Fig. 5(b) shows the fatigue characteristic of Au/PZT/YBCO/MgO thin film. After 10⁷ times of switching, the remnant polarization 2P_r decreased rapidly. This decreasing rate is slower than that of the Au/PZT/Pt/MgO thin film, but it still should be improved for applications.

Incomplete crystallization of PZT thin films is responsible for low switching characteristics of Au/PZT/YBCO capacitors. To improve the crystalline property of PZT, we are trying new substrates with a better matching of PZT, YBCO and substrate lattices.

4. Conclusion

We investigated the crystallization and ferroelectric properties of the Pb₅(Zr₀.₅₂Ti₀.₄₈)O₃ thin films on Pt and
YBCO bottom electrodes. The Au/PZT/Pt/MgO thin films have a remarkable perovskite (00l) structure only prepared at a substrate temperature of 650 °C. Whereas Au/PZT/Pt/MgO thin films have a narrow temperature range for the perovskite (00l) structure, Au/PZT/YBCO/MgO thin films exhibit a wide processing temperature range from 550 to 680 °C. Au/PZT/YBCO/MgO thin films indicated a better ferroelectric performance than Au/PZT/Pt/MgO thin films. Because of these results, it is clear that the YBCO bottom electrode is suitable for PZT thin films. Nevertheless, the remnant polarization of the Au/PZT/YBCO/MgO thin film was reduced to half after about $10^8$ cycles of switching.

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References