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Investigation on $F_{R(LT)}$–$F_{R(HT)}$ phase transition and pyroelectric properties of pulsed laser deposited $Pb(Zr_{0.93}Ti_{0.07})O_3$ thin films

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ABSTRACT

The preparation process, crystallinity and electrical properties of pulse laser deposited $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films were investigated in this paper. PZT ($x = 0.93$) thin film samples deposited at different substrate temperatures were prepared. Si (1 1 0) was the substrate; Ag and YBCO were the top electrode and the bottom electrode respectively. The bottom electrode YBCO was deposited on the Si substrate by pulsed laser deposition (PLD), and then PZT was epitaxially deposited on YBCO also by PLD. After annealing, the top electrode Ag was prepared on PZT by thermal evaporation, and then the Ag/PZT/YBCO/Si structured thin films were obtained. The XRD and the analysis of their electrical characters showed that, when the substrate temperature was elevated from 600 °C to 800 °C, the crystallinity and electrical properties of PZT thin films became better and better, and the $F_{R(LT)}$–$F_{R(HT)}$ phase transition of PZT ($x = 0.93$) thin films occurred at 62 °C. The PZT film deposited at 800 °C had the best pyroelectric properties, and when the $F_{R(LT)}$–$F_{R(HT)}$ phase transition of this film occurred, the peak value of pyroelectric coefficient (p) was obtained, with a value of 1.96×10^{-6} C/(cm^2 K). The PZT film deposited at 800 °C had the highest remnant polarization (P_r) and the lowest coercive field (E_c), with the values of 34.3 μC/cm^2 and 41.7 kV/cm respectively.

1. Introduction

In the past few decades, infrared detection and the thermal imaging have been used for both military and non-military applications; such as night vision, target acquisition, missile guidance, automotive vision enhancement, fire detection and medical diagnostics [1,2]. For these applications, efforts have been made to develop uncooled infrared and imaging devices. Lead zirconate titanate (PZT) is a perovskite structure ferroelectric material with excellent piezoelectric, ferroelectric and pyroelectric properties; and these properties can be improved by changing the ratio of Zr/Ti and doping [3–6]. The Zr-rich (Zr > 90 mol%) PZT has a low temperature rhombohedral ($F_{R(LT)}$)–high temperature rhombohedral ($F_{R(HT)}$) ferroelectric phase transition and a large spontaneous polarization [7,8]; when the $F_{R(LT)}$–$F_{R(HT)}$ phase transition is induced by temperature, a nonlinear change of spontaneous polarization occurs, and a large pyroelectric coefficient (p) is obtained, which can be used for heat–electric conversion such as infrared detector and thermal imaging [1,2,6,9,10]. When the $F_{R(LT)}$–$F_{R(HT)}$ phase transition happens, the dielectric constant (ε) and dielectric loss ($\tan\delta$) are low, and therefore the figure of merit, F_d, as given by

$$F_d = \frac{p}{C_v(\varepsilon \cdot \tan\delta)^{1/2}}$$

is large, where C_v is the molar heat capacity under constant volume. Consequently Zr-rich PZT thin films can be widely used in uncooled infrared detection. Compared to other heat–electric infrared detector, the Zr-rich PZT infrared detector made using $F_{R(LT)}$–$F_{R(HT)}$ phase transition of it can work at room temperature; the $F_{R(LT)}$–$F_{R(HT)}$ phase transition temperature of PZT is much lower than its curie temperature, it will not depolarize and need not be repolarized after each working cycle.

$YBa_2Cu_3O_{7-\delta}$ (YBCO) has been used as the electrode materials of PZT thin films in recent years. It has many advantages than precious metals Pt and Au, such as low lattice mismatch with PZT, and PZT thin films can grow epitaxially on it easily. YBCO also has excellent electrical conductivity and strong thermal stability. Therefore YBCO is an excellent electrode material for PZT thin films, and special attention has therefore been paid to it, with many investigations on PZT/YBCO heterojunctions having been reported [11,12].

In Ref. [13], we had investigated the influence of annealing temperature on the crystalline structure and electrical properties of $Pb(Zr_{0.95}Ti_{0.05})O_3$ thin films. The results showed that, the $Pb(Zr_{0.95}Ti_{0.05})O_3$ thin film annealed at 650 °C had better crystalline structure and electrical properties than the ones annealed at 600 °C and 550 °C. The $F_{R(LT)}$–$F_{R(HT)}$ phase transition temperature of the

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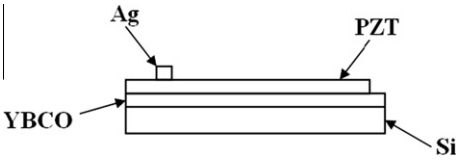

Fig. 1. Ag/PZT/YBCO/Si structured thin film.

$Pb(Zr_{0.95}Ti_{0.05})O_3$ thin film annealed at 650 °C was about 50 °C, and the pyroelectric coefficient at this temperature was 3.5×10^{-8} C/(cm^2 K). In this work, Ag/PZT ($Pb(Zr_{0.93}Ti_{0.07})O_3$)/YBCO ($YBa_2Cu_3O_{6.5}$)/Si structured thin films (showed in Fig. 1) deposited at different substrate temperatures from 600 °C to 800 °C were prepared. The PZT and YBCO targets were prepared by Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences. An YBCO buffer layer was deposited on the Si substrate first, and then PZT thin film was epitaxially deposited on it. After annealing, the top electrode Ag was prepared on PZT by thermal evaporation, and then the Ag/PZT/YBCO/Si structured thin films were obtained. The crystalline structures of the PZT thin films were analyzed by X-ray diffraction (XRD), and the ferroelectric and pyroelectric properties were also measured. The preparation process and the influence of the preparation process on the crystalline structure and electrical properties of PZT thin films were investigated.

2. Experimental procedures

The PZT film and YBCO buffer layer were prepared by PLD. The laser source was a KrF pulsed excimer laser, the maximum output energy and wavelength of the laser were 750 mJ/pulse and 248 nm respectively. The PZT target was a high-temperature sintering Zr-rich PZT ceramic, and the Zr/Ti ratio of the target was 93/7. The YBCO target was also a high-temperature sintering ceramic with an excellent electrical conductivity, and the composition of it was $YBa_2Cu_3O_{6.5}$; the resistance of it at room temperature was less than 10^{-3} Ω. The PZT and YBCO targets were purchased from (Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences). Si (1 1 0) was the substrate; YBCO and Ag were the bottom electrode and the top electrode respectively. The background pressure of the vacuum chamber was less than 10^{-4} Pa using a mechanical pump and turbo-molecular pump, and then O_2 was introduced into the vacuum chamber. During deposition of the YBCO buffer layer, the O_2 pressure was 26 Pa, the substrate temperature was 800 °C, the energy of each laser pulse was 300 mJ, the repetition frequency was 8 Hz, and deposition time was 40 min. Following deposition, the YBCO bottom electrode films were annealed at 800 °C and 26 Pa O_2 pressure for 10 min. For deposition of the PZT thin films, the O_2 pressure was 14 Pa, the substrate temperatures were from 600 °C to 800 °C, the energy of each laser pulse was 300 mJ, the repetition frequency was 8 Hz, and deposition time was 50 min. Then the film samples were annealed at 700 °C and 100 Pa O_2 pressure for 20 min. The distance between target and substrate was kept at 50 mm throughout. X-ray diffraction (X'TRA, ARL, Switzerland) was used to analyze the crystallinity of YBCO and PZT thin films. The ferroelectric properties of the four PZT thin film samples B–E were analyzed by a ferroelectric test system (TD-88A). The pyroelectric coefficients of the

Table 1
Preparation process of YBCO bottom electrode thin film.

Deposition conditions	800 °C, 26 Pa, 300 mJ/pulse, 8 Hz, 40 min
Annealing conditions	800 °C, 26 Pa, 10 min

Table 2
Preparation process of five PZT thin film samples.

Sample	A	B	C	D	E
Substrate temperature	600 °C	650 °C	700 °C	750 °C	800 °C
Other deposition conditions	14 Pa, 300 mJ/pulse, 8 Hz, 50 min				
Annealing conditions	700 °C, 100 Pa, 20 min				

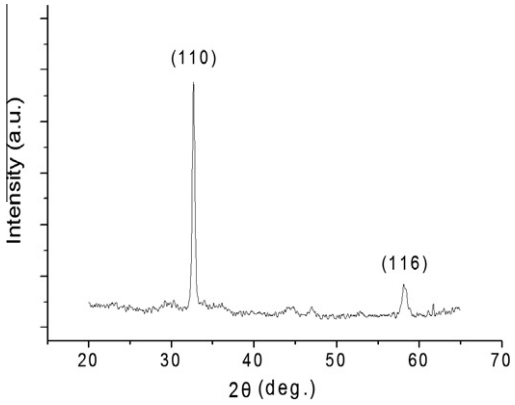

Fig. 3. XRD pattern of the YBCO bottom electrode thin film (the peaks of Si have been omitted).

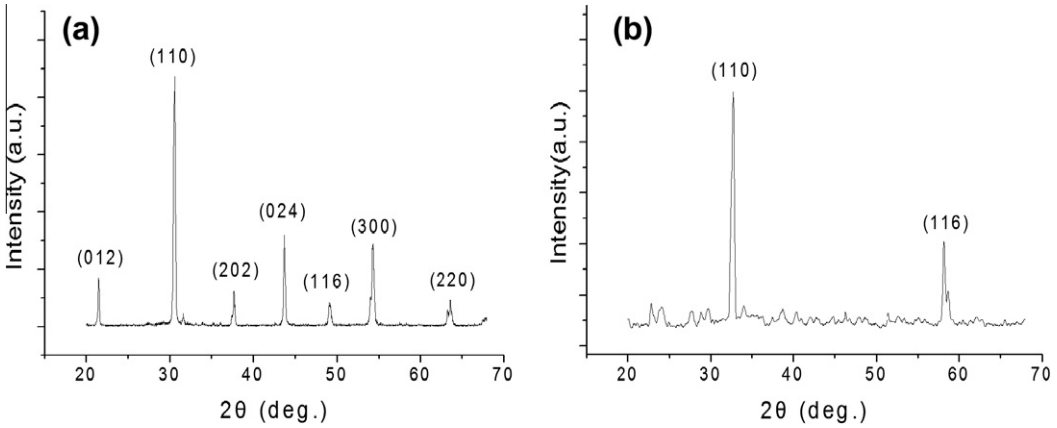

Fig. 2. XRD patterns of (a) $Pb(Zr_{0.93}Ti_{0.07})O_3$ target and (b) YBCO target.