Applied Surface Science 255 (2009) 4197–4200

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Electric and ferroelectric properties of PZT/BLT multilayer films prepared by photochemical metal-organic deposition

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ARTICLE INFO

Article history:
Received 13 June 2008
Received in revised form 27 August 2008
Accepted 4 November 2008
Available online 12 November 2008

PACS:
77.84.−s (Ferroelectric materials)
73.21.Ac (Multilayers)

Keywords:
PZT
BLT
Multilayer film
Direct patterning
Fatigue-free

ABSTRACT

The electric and ferroelectric properties of lead zirconate titanate (PZT) and lanthanum-substituted bismuth titanate (BLT) multilayer films prepared using photosensitive precursors were characterized. The electric and ferroelectric properties were investigated by studying the effect of the stacking order of four ferroelectric layers of PZT or BLT in 4-PZT, PZT/2-BLT/PZT, BLT/2-PZT/BLT, and 4-BLT multilayer films. The remnant polarization values of the 4-BLT and BLT/2-PZT/BLT multilayer films were 12 and 17 $\mu C/cm^2$, respectively. Improved ferroelectric properties of the PZT/BLT multilayer films were obtained by using a PZT intermediate layer. The films which contained a BLT layer on the Pt substrate had improved leakage currents of approximately two orders of magnitude and enhanced fatigue resistances compared to the films with a PZT layer on the Pt substrate. These improvements are due to the reduced number of defects and space charges near the Pt electrodes. The PZT/BLT multilayer films prepared by photochemical metal-organic deposition (PMOD) possessed enhanced electric and ferroelectric properties, and allow direct patterning to fabricate micro-patterned systems without dry etching.

1. Introduction

Ferroelectric thin films have received considerable interest in recent decades due to potential applications in ferroelectric random access memory and microelectromechanical systems [1,2]. Among related materials of interest, lead zirconate titanate (PZT) has been intensively investigated due to its large remnant polarization (P_r) and small coercive field (E_c) [1]. However, PZT films with Pt electrodes suffer from fatigue in which the P_r declines after about 10^8 switching cycles [3,4]. On the other hand, lanthanum-substituted bismuth titanate (BLT) films have become attractive due to their large polarization compared to strontium bismuth tantalate (SBT) and much better fatigue behavior when compared to conventional lead-based materials [5,6]. Therefore, PZT/BLT multilayer films are of interest as they may provide improved ferroelectric properties such as a large P_r, a small E_c, and excellent fatigue resistance.

There are several issues that should be overcome to realize the integration of ferroelectric thin films into electronic devices. One of the issues is establishing etching technology to eliminate harmful etching damage [7]. During dry etching, changes in the physical and electrical properties of PZT films due to reactive free radicals and ions in the plasma have been reported [8,9]. Also, Kim et al. reported that Ar ion bombardment and chemical reaction have a degrading effect on the ferroelectric properties, cause destruction of the crystalline structure of BLT films, and create nonvolatile etch by-products such as La-chlorides [10,11]. Photochemical metal-organic deposition (PMOD) has been studied in order to minimize undesirable etching damage. PMOD lithographically produces a patterned structure without using a photoresist or dry etching because of the photosensitive nature of the precursors [12,13]. After lithographic exposure, film development can be performed by rinsing in a solvent to remove the unexposed part of the coated film, leaving a patterned structure.

In this work, a direct patterning method for the lithographic deposition of PZT/BLT multilayer films formed by PMOD is reported and the effects of the stacking order on the electric and ferroelectric properties of the resulting PZT/BLT multilayer films were investigated.

2. Experimental procedure

The precursors used for the photochemical production of PZT films were lead 2-ethylhexanoate, zirconyl 2-ethylhexanoate, and titanium isopropoxide. These precursors were dissolved in hexane.

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doi:10.1016/j.apsusc.2008.11.011

The atomic ratio of Zr:Ti was fixed at 52:48. A 15% excess of Pb was added for the compensation of Pb loss during high temperature annealing [14]. The photosensitive starting precursors for the BLT were bismuth 2-ethylhexanoate, lanthanum 2-ethylhexanoate, and titanium isopropoxide. A 10% excess of bismuth 2-ethylhexanoate was added to compensate for the loss of Bi during high temperature annealing [15]. PZT and BLT precursors were spin-coated at 2000 rpm for 30 s on two different types of substrates. One substrate was chemically cleaned Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) used for measuring the electric and ferroelectric properties and the other substrate was p-Si(1 0 0) wafer used to demonstrate the direct patterning process of 200 nm thick PZT and BLT films by PMOD.

The precursor films for lithography were exposed to the output of a 1000 W mercury arc lamp passed through a chrome mask for 15 min. The latent image was developed with a solvent rinse to reveal a negative pattern. The resultant film was annealed for 10 min at 400 and 600 °C. This process was repeated for each layer. Each of the multilayer film structures were annealed at 700 °C for 1 h under ambient O_2. The single layer thicknesses of PZT and BLT were around 95 nm as measured using an ellipsometer and the final thickness of the ferroelectric layers was uniform regardless of the stacking order of the PZT and BLT layers. In order to measure the electric and ferroelectric properties of the films, a 150 nm thick Pt top electrode with a 200 μm diameter was sputter-deposited on the 380 nm thick PZT/BLT multilayer films. The ferroelectric properties of the films were measured using a RT66A (Radiant Technology) ferroelectric tester with a pulse width of 0.15×10^{-3} s and the current–voltage (*I*–*V*) characteristics of the films were obtained using a HP 4145B (Hewlett Packard) with a holding time of 0.4 s and a step of 0.5 V. The direct patterning images of the films were observed by using a scanning electron microscope (SEM) and optical microscopy. The phase formation and crystallinity of the films were studied with an X-ray diffractometer (XRD) using Cu kα radiation.

3. Results and discussion

XRD spectra of the various PZT/BLT multilayer films coated on Pt(1 1 1)/Ti/SiO_2/Si substrates are shown in Fig. 1. All of the diffraction peaks of the PZT/BLT multilayer films correspond to PZT, BLT, and Pt. The 4-PZT film was crystallized with a preferred <1 1 1> orientation due to (1 1 1) plane matching between Pt and PZT. This highly preferred orientation indicates that the nucleation and growth of PZT is strongly affected by the Pt substrate [16]. However, the diffraction intensities of BLT showed a distribution similar to BLT ceramics [17] and Pt (1 1 1) was not found to influence the growth orientation of the BLT films [18].

An enhancement of the (1 0 0) PZT diffraction peak intensity was observed in the PZT/2-BLT/PZT film as compared to the 4-PZT film. However, the BLT peak intensity distribution of the PZT/2-BLT/PZT film was not different than that of the 4-BLT film. These results confirmed that neither the Pt (1 1 1) substrate nor the (1 1 1)-oriented PZT film showed an influence on the growth orientation of the BLT film. This enhancement of the (1 0 0) PZT diffraction peak was observed from the upper-most top PZT layer because the (1 0 0) growth plane of PZT has the lowest activation energy [19]. Also, the BLT/2-PZT/BLT film showed a more enhanced (1 0 0) PZT diffraction peak intensity compared to the PZT/2-BLT/PZT film because the growth orientation of the 2-PZT intermediate layers was not affected by either the bottom BLT layer or the Pt substrate. This result implies that the bottom ferroelectric layer, which is the first layer deposited on the Pt substrate, has a significant influence on the growth orientation of the entire film.

P–*E* hysteresis loops of the various PZT/BLT multilayer films subjected to an applied voltage of 15 V are shown in Fig. 2. In the case of the 4-PZT and 4-BLT films, the P_r values were 31 and 12 μC/cm^2 while the E_c values were 53 and 101 kV/cm, respectively. The 4-PZT film showed higher P_r and lower E_c values than the 4-BLT film because PZT domains are relatively easier to switch than bi-layered perovskite domains [20]. Namely, upon the application of the electric field, the PZT film shows more displacements of ions and charge defects than the BLT film. In the case of the PZT/2-BLT/PZT and BLT/2-PZT/BLT films, the P_r values were 21 and 17 μC/cm^2 while the E_c values were 67 and 84 kV/cm, respectively. In the case of the PZT films, it is well known that the coexistence of rhombohedral and tetragonal phases is commonly observed around the morphotropic phase boundary (MPB) at a Zr:Ti ratio of 52:48 [21,22]. The MPB composition of the PZT films tends to move towards a rhombohedral phase, a Zr-rich side, under the influence of in-plane film stress, regardless of whether it is tensile or compressive [21,22] and the spontaneous polarization direction of rhombohedral PZT is [1 1 1] [23]. In our case, as shown in Fig. 1, the PZT in the PZT/2-BLT/PZT film showed a relatively higher <1 1 1> growth orientation than in the BLT/2-PZT/BLT film. Namely, due to the increase of <1 1 1> spontaneous polarization,

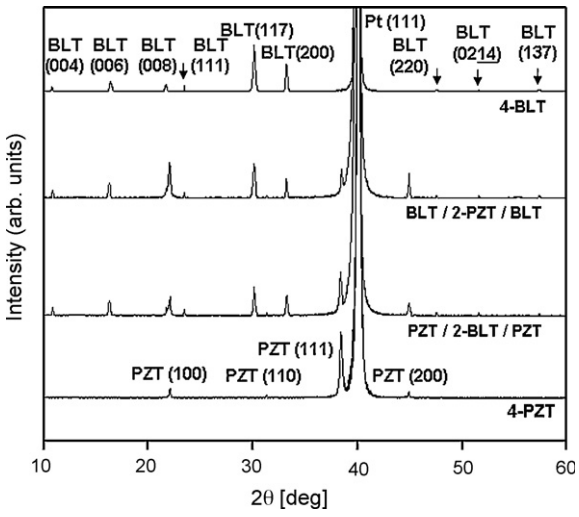

Fig. 1. XRD spectra of the PZT/BLT multilayer films annealed at 700 °C: 4-PZT, PZT/2-BLT/PZT, BLT/2-PZT/BLT, and 4-BLT films.

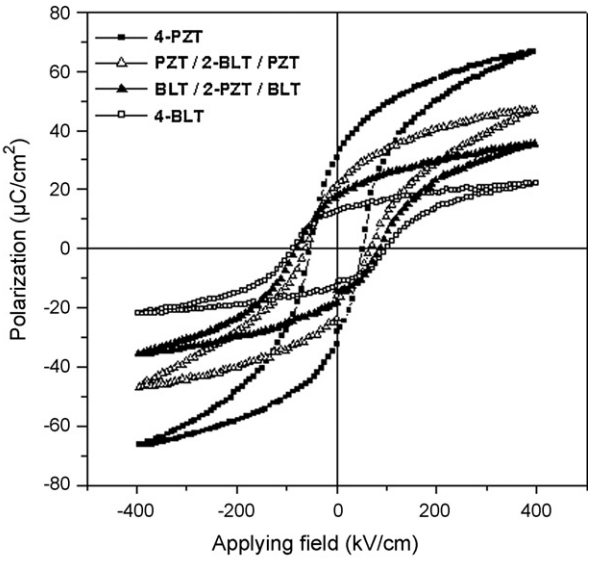

Fig. 2. *P*–*E* hysteresis loops of the PZT/BLT multilayer films annealed at 700 °C: 4-PZT, PZT/2-BLT/PZT, BLT/2-PZT/BLT, and 4-BLT films.