Effects of switching pulse width and stress on properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films*

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Polycrystalline ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films are prepared on $Pt/Ti/SiO_2/Si$ substrates by the conventional metalorganic decomposition method. It is observed that with the increase of switching pulse width, the remnant polarisation and the coercive field increase. A wider switching pulse can result in poorer fatigue properties, which comes from more charged defects diffusing to and being trapped on domain walls. On the other hand, when the compressive stress is applied to films, the fatigue properties can be improved. This phenomenon is due to the reorientation of domains under stress.

Keywords: ferroelectric films, polarisation, domains
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1. Introduction

During the last decades, with the quick development of electronic techniques and the information industry, ferroelectric memory has attracted much attention due to its fast read-write speed, high density, and non-volatile characteristics.[1−4] Recently, bismuth layer-structured ferroelectric thin films (BLSFs), such as La-doped $Bi_4Ti_3O_{12}$ thin films ($Bi_{4-x}La_xTi_3O_{12}$),[5,6] owing to their lower processing temperature and outstanding ferroelectric properties, have aroused considerable interest.

Switching pulse width and stress are two important factors that can affect the properties of films.[7−9] It is reported that the switching pulse width can influence the ferroelectric properties of thin films.[7] Stress exists widely in films, which results from the mismatching of the lattice parameters and the thermal expansion constant between substrates and films, forming and disappearing of grain boundaries during the film growth and the succeeding integrating process and so on.[10] Stress in films can greatly affect the ferroelectric,[11] piezoelectric[12] and dielectric[13] properties of the thin films. Therefore, studying the effects of the switching pulse width and stress in films is crucial to the further applications of ferroelectric materials and to providing the possibility of the improvement of these materials. In the present paper, we mainly report on the effects of switching pulse width and stress on the properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films, and further clarify the main cause for these effects.

2. Experiment

BLT thin films were deposited on $Pt/Ti/SiO_2/Si$ substrates by the metalorganic decomposition (MOD) method using $Bi(NO_3)_3{\cdot}5H_2O$ (10% excess to compensate for Bi loss during high-temperature treatment), La_2O_3 and $Ti(OC_4H_9)_4$ as the precursors. The solution of $Bi(NO_3)_3{\cdot}5H_2O$ dissolved in glacial acetic acid was first mixed with the solution of La_2O_3 dissolved in nitric acid in an appropriate ratio. Then a certain amount of $Ti(OC_4H_9)_4$ was added into the above solution, and ethylene glycol monomethyl ether was used to achieve a concentration of 0.1 mol/L. Finally a small amount of acetylacetone was adopted to stabilise the solution. The resulting solution was then spin-coated onto $Pt/Ti/SiO_2/Si$ substrates at a speed of 3500 rps followed by a dry process at 250 °C for 1 min and then at 400 °C for 3 min to remove or-

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ganic compounds. The above described process was repeated 4 times in order to achieve a desired thickness of about 360 nm. The newly formed multilayer films were annealed at 700 °C for 1 h in oxygen ambience. The Pt top electrodes, with a size of 0.0314 mm^2 or so, were deposited by sputtering. Finally, a post-annealing procedure at 600 °C for 10 min in O_2 atmosphere was used to ensure good contact between Pt electrodes and films.

A wafer flexure system was designed to apply uniaxial compressive stress along the film surface. One end of the strip-shaped sample was clamped, while the other end could be raised by an improved micrometer. Film stress was calculated by using the elastic bending theory[14] with the modulus of $Bi_4Ti_3O_{12}$ ceramics given by Jiménez *et al.*[15] The structural characterisations and the surface morphology observations were carried out by x-ray diffraction (XRD, D/Max-RB)) and atomic force microscopy (AFM, Nano IV, Veeco Co.), respectively. Ferroelectric and fatigue properties were measured by using the standard ferroelectric tester RT66A. Each experimental result was repeated at least 4 times.

3. Results and discussion

Figure 1 shows the XRD patterns of the BLT films annealed at 700 °C, which indicates that the film has a typical bismuth-layered perovskite structure. The lattice constants investigated from XRD are $a = 5.406$ Å, $b = 5.417$ Å, and $c = 32.704$ Å (1 Å=0.1 nm).

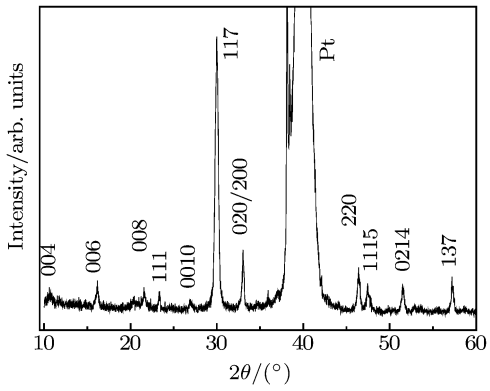


Fig. 1. XRD patterns of BLT thin film annealed at 700 °C.

The surface morphology of BLT thin film, examined by AFM over an area of 3 μm×3 μm displayed in Fig. 2, indicates that the film surface is uniform. The root mean square (RMS) roughness is about 13 nm.

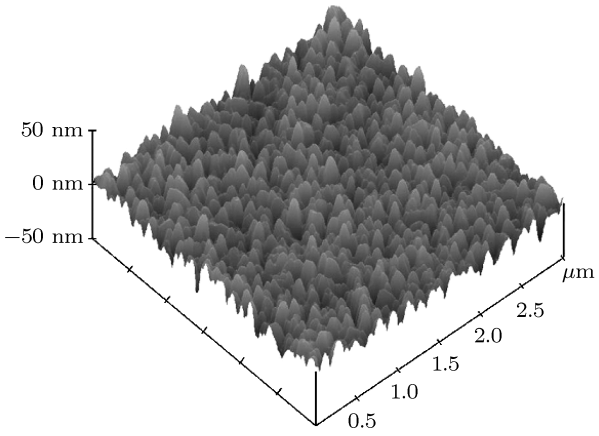


Fig. 2. AFM surface morphology of the BLT film.

Figure 3(a) presents the polarisation-field hysteresis loops of BLT thin films measured at various switching pulse widths. The inset shows the ferroelectric polarisation test scheme, in which τ and V represent the pulse width and the pulse magnitude of the applied field, respectively. In this experiment, V was kept at 420 kV/cm. To compare the effect of different τ on the remnant polarisation (P_r) and the coercive field (E_c), the values of P_r and E_c measured

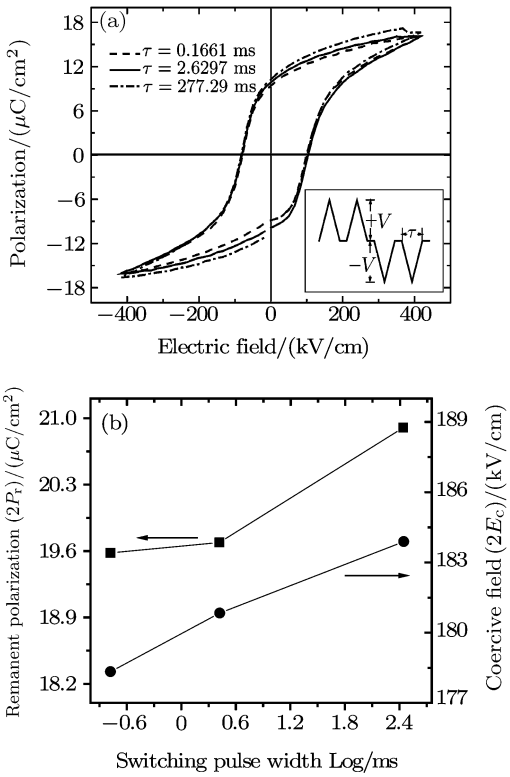


Fig. 3. P–E hysteresis loops (a) and the values of $2P_r$ and $2E_c$ (b) of BLT thin films measured at different switching pulse widths. The maximum measured electric field is 420 kV/cm. The inset shows the ferroelectric polarisation test schemes.

at different values of τ were taken out as shown in Fig. 3(b). With the value of τ increasing from 0.1661 to 277.29 ms, the remnant polarisation and the coercive field increase from 19.6 to 20.9 μC/cm^2 ($2P_r$) and from 178 to 184 kV/cm ($2E_c$), respectively. The reason for the increase of both P_r and E_c with τ is easy to understand. With the value of τ increasing, the moving distance of new domain walls becomes longer. Hence, more polarisation can switch and P_r increases. As for E_c, it reflects the coercive character of switchable domains. Except 180° domains, 90° domains exist in BLT.[16] The 90° domain reversal is more difficult than 180° domain switching.[17,18] With the value of τ increasing, the 90° domains, which cannot be reversed originally at narrower pulse width, may complete the polarisation switching and result in the increase of E_c.

It is known that BLT films have excellent fatigue-endurance behaviour when measured at higher switching frequency (at 1 MHz) as reported by Bae *et al.*[6] while when measured at lower switching frequency (such as 50 kHz),[18,19] the films show poor fatigue behaviour. To compare the fatigue behaviours of BLT films under stress measured at two different switching pulse widths (7.6 μs and 8.6 μs), the switching frequency was kept at 50 kHz. The results are shown in Fig. 4. The inset in Fig. 4(a) shows the ferroelectric fatigue test schemes. The values of τ_1 and τ_2 are the switching pulse width and switching period, respectively. The switching field and switching period τ_2 were kept at 220 kV/cm and 20 μs (i.e. switching frequency is 50 kHz), respectively. Two points might be worth mentioning.

(i) When films are measured in the free state, after about 10^8 cycles, the non-volatile polarisation drops to about 65% of its initial value for the switching pulse width of 7.6 μs while that about 45 % for 8.6 μs, which means that the fatigue behaviour is strongly dependent on the switching pulse width. The wider the switching pulse width is, the faster the fatigue rate will be. The pinning of domain walls by charged defects (such as oxygen vacancies),[20,21] as one of the most important origins of fatigue, is put forward as an explanation. During the domain switching, charged defects can diffuse and finally be trapped at domain boundaries because of the energetically favourable condition (i.e. minimised free energy).[7,22] Under the wider switching pulse width, the diffusing distance of the charged defects will become longer. Hence, the charged defects, which cannot diffuse to the domain walls at narrower pulse width, can diffuse to the domain walls at wider pulse width. Therefore, more domain walls can be pinned, which can result in more distinct degradation of the nonvolatile polarisation during polarisation switching at wider pulse width. The same results were also observed by Zhang *et al.*[7] in SBT thin films.

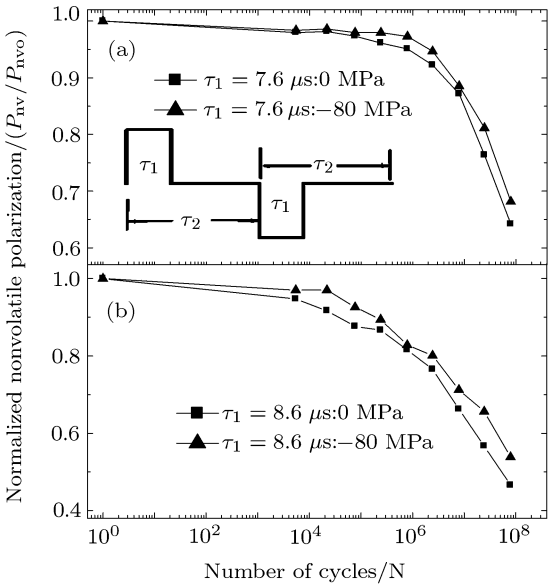


Fig. 4. Non-volatile polarisations with switching cycles of BLT films under different stresses measured at two different switching pulse widths of 7.6 μs (a) and 8.6 μs (b). The inset shows the ferroelectric fatigue test schemes.

(ii) When compressive stress (shown by a minus sign) is applied to the samples, the fatigue properties of films are improved, measured at the switching pulse width of either 7.6 μs or 8.6 μs. This phenomenon can be explained by stress-induced domain reorientation. For Bi-layered perovskite, the polarisation is mainly along the shortest a axis.[11] When the compressive stress is applied along the film surface, the domains originally perpendicular to the out-of-plane may easily turn to the direction parallel to the in-plane.[11] This reorientation can lead the domains parallel to the compressive stress to grow larger.[19] Namely, domains become coarse under stress, which was also observed in $PbTiO_3$ thin films by Ren *et al.*[23] and in $BaTiO_3$ single crystals by Munoz-Saldana *et al.*[24] It is known that one of the main causes of fatigue is domain wall-pinning by charged defects.[25] The coarsening of domains, induced by stress, can reduce the density of the domain walls, and further can reduce the pinning probability of domain walls by charged defects. Therefore, the fatigue behaviour can be improved under stress.

4. Conclusions

BLT thin films are successfully deposited on $Pt/Ti/SiO_2/Si$ substrates by the conventional metalorganic decomposition method. It is found that with the switching pulse width increasing from 0.1661 to 277.29 ms, the remnant polarisation and the coercive field increase from 19.6 to 20.9 $\mu C/cm^2$ ($2P_r$) and from 178 to 184 kV/cm ($2E_c$), respectively. On the other hand, the films show a good fatigue resistance at a switching pulse width of 7.6 μs compared with that at 8.6 μs. The fatigue properties can be improved by stress, which is owing to the reorientation of domains under stress.

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