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Polarization fatigue and photoinduced current in $(Pb_{0.72}La_{0.28})Ti_{0.93}O_3$ buffered $Pb(Zr_{0.52}Ti_{0.48})O_3$ films on platinized silicon

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ABSTRACT

We report a study on the fatigue behavior of $Pb(Zr_{0.52}Ti_{0.48})TiO_3$ (PZT) films deposited on $Pt/Ti/SiO_2/Si$ substrates by a sol–gel method with single- and double-sided $(Pb_{0.72}La_{0.28})Ti_{0.93}O_3$ (PLT) buffer layers, with an attempt to clarify the role of the top and bottom PLT buffer layers on the fatigue endurance (FE) of the PZT films. It is revealed that the existence of the PLT buffer layer and the level of driving alternating-current electric switching field strongly influence the fatigue properties. In terms of the existence of an asymmetric built-in electric field near the top and bottom interfaces between the film and metal electrode, we explain the observed fatigue properties.

1. Introduction

Lead zirconate titanate (PZT) films have been widely studied in recent years as promising materials for making nonvolatile ferroelectric random access memories due to their large remnant polarization and relatively low processing temperature. However, the problem of fatigue, defined as the loss of switchable polarization by alternating-current (ac) field, prohibits commercial use of PZT films [1,2]. The use of oxide electrodes instead of Pt, such as RuO_2, IrO_2, $La_{0.5}Sr_{0.5}CoO_3$ and $SrRuO_3$ (SRO), has proven to be effective for improving the fatigue of PZT films [3–9]. According to many researchers, good fatigue endurance (FE) can only be achieved if the oxide electrodes or buffer layers were used on both sides of PZT films. There were also several intriguing results reported in the literature. For example, Nakamura et al. [10] showed that the fatigue-free behavior can be obtained in an asymmetrical capacitor configuration $IrO_2/PZT/Pt$ (we use top/film/bottom representation for the film capacitor structure). The fatigue-free behavior was also observed in the SRO buffered PZT films, where the FE was determined only by the top interface as long as the driving field was above a critical value [11]. In order to understand physical origin of the interface dependent fatigue behavior, one must conduct a systematic study on different oxide/PZT/oxide structures.

Recently, La-modified lead titanate $(Pb_{1-x}La_x)Ti_{1-x/4}O_3$ solid solution has been identified as a good candidate for the buffer layer to improve the FE of the PZT films [12,13]. It was pointed out that the buffer layer can play a critical role in compensating charges accumulated at the interfaces, attributed to the aliovalent substitution of La^{3+} for Pb^{2+}, which led to enhanced fatigue properties of the PZT films. However, previous studies found that the FE was improved only when the PLT buffer layers were used on both sides of a PZT film, whereas the PZT film with only a PLT bottom buffer layer did not have a good FE [12]. Therefore, it remains unclear at present whether the FE of PZT film is only controlled by the top interface or by both bottom and top buffer layers. To clarify this question, we fabricated a series of PLT buffered PZT films with different configurations and studied their fatigue properties under different levels of ac driving fields.

The photo-response of ferroelectric film has been studied because of its potential application, such as in the area of optoelectronic devices [14]. When a ferroelectric film is illuminated after electric poling, short-circuit current can be generated due to the separation of photoinduced electrons and holes by its internal electric field. This internal electric field is closely related to the Schottky barriers on the film/electrode interfaces, in addition to the alignment of polarization [14,15]. Thus there may exist some correlations between the photoinduced current and the fatigue

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properties, because both are associated with the interfaces of the metal-film-metal structure. In this study, we performed the measurement of the photoinduced current, with an attempt to explain the fatigue behaviors.

2. Experimental

Both PLT buffer layer and PZT film were deposited on the Pt/Ti/SiO_2/Si(100) substrate via a sol–gel technique. In particular, we prepared four PLT or PZT buffered PZT films, PZT/PZT/PZT, PLT/PZT/PZT, PZT/PZT/PLT, and PLT/PZT/PLT. The starting materials for the PZT solution were zirconium propoxide, titanium propoxide, and lead acetate. They were dissolved in 2-methoxytheanol and glacial acetic acid, and then mixed in the stoichiometric ratio of Pb:Zr:Ti = 1.10:0.52:0.48 in which 10% excess Pb was to compensate the loss of Pb during the sintering process. The PLT solution with 10% excess Pb was prepared using the same method as the PZT solution. The starting materials were lanthanum nitrate, titanium propoxide and lead acetate. For the buffer layers, the parent PLT and PZT solutions were diluted to 0.08 ML^{-1} with 2-methoxytheanol. The deposited bottom PLT or PZT buffer layer was fired at 400 °C for 0.5 h, and then annealed at 550 °C for 1 h. The thicknesses of the buffer layers were about 12 nm. The PZT films were prepared via a spin-coated method with 0.2 ML^{-1} solution. The PZT film with each coating was fired at 400 °C for 0.5 h. After such coating and heating were carried out nine times, the top buffer layer began to be coated. Finally, the whole film was annealed at 650 °C in air for 1 h.

The thicknesses of all prepared films were about 380 nm, which were determined by a surface profilometer and compared against the values taken from the scanning electron microscopy cross-section images. For electrical measurements, Pt dots with diameters of 0.28 mm were sputtered onto the films, forming a typical metal-film-metal capacitor structure. The crystal structures of the films were evaluated by measuring X-ray diffractometer (XRD) spectra with Ni filtered CuK_α radiation. Hysteresis loops and fatigue properties were examined using a Radiant Precision Ferroelectric Analyzer. Short-circuit photocurrent (PHC) under a UV light (produced by UV lamp) illumination was measured on a Keithley 6517A electrometer with careful electrical isolation.

3. Results and discussion

We first checked the effect of the buffer layer on microstructures of the PZT films. Fig. 1 shows the XRD patterns for the buffered PZT films along with that of a pure PZT film. It can be seen

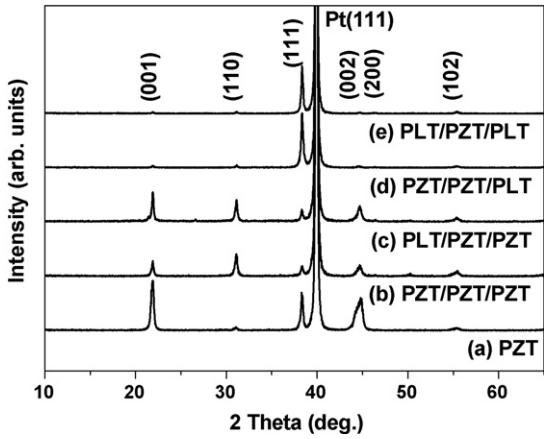

Fig. 1. XRD patterns of the PZT films with and without PLT or PZT buffer layers.

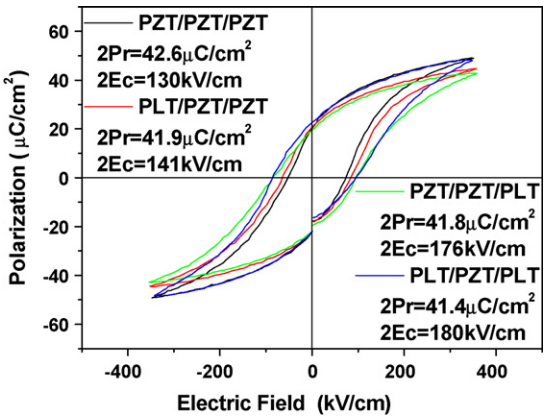

Fig. 2. Electric hysteresis loops of the PZT films with 12-nm-thick PLT or PZT buffer layers. The corresponding film configurations are: (a) PZT/PZT/PZT, (b) PLT/PZT/PZT, (c) PZT/PZT/PLT, and (d) PLT/PZT/PLT.

that the PZT film without the buffer layer shows distinct (0 0 1) and (1 1 1) peaks, and a weak (1 1 0) peak. The 12 nm-thick PZT bottom buffer layer increases the intensity of the (1 1 0) peak, as shown in Fig. 1(b) and (c). Cattan et al. [16] found the similar phenomenon in PZT films buffered by a $PbTiO_3$ (PT) layer, which was attributed to a diffracting plane of the pyrochlore phase in the PT buffer layer. The PLT bottom buffer layer leads to preferred 1 1 1) orientation of the PZT film as can be seen in Fig. 1(d) and (e). This result is consistent with that reported by Lee et al. [12]. We checked the XRD spectra of the PLT and PZT buffer layers and found that they had 1 1 1) and (1 1 0) preferred orientations, respectively, indicating that the orientation of the buffered PZT film was dependent on that of the bottom buffer layer.

The electric hysteresis loops of the PZT and PLT buffered PZT films are shown in Fig. 2. In comparison to the pure PZT film, which has a remnant polarization 2Pr = 46.3 μC/cm^2 and a coercive field 2Ec = 110 kV/cm, all buffered PZT films show slightly smaller 2Pr values but much higher 2Ec values. The smaller 2Pr values may be due to the paraelectric nature of the PLT layers which are in series-connection with the PZT film. The increase of the coercive field was also reported in $(Ba_{0.5}Sr_{0.5})TiO_3$ buffered PZT films, which was explained in terms of the effect of the complex interface between the film and electrodes [17]. In addition, the ferroelectric properties are strongly related to the orientation of films. It was noted

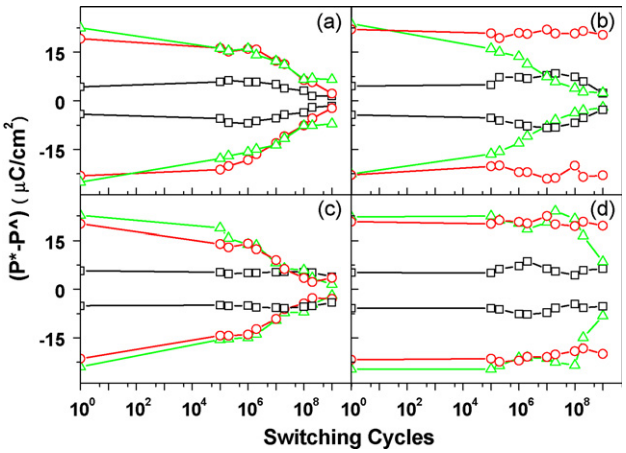

Fig. 3. Fatigue endurance tests under different driving fields of 1.5Ec (squares), 3Ec (circles), and 5Ec (triangles). P* is the switched polarization and P^ is the non-switched polarization. The corresponding film configurations are: (a) PZT/PZT/PZT, (b) PLT/PZT/PZT, (c) PZT/PZT/PLT, and (d) PLT/PZT/PLT.

that Ec for the samples with bottom PZT buffer layer was lower than those with bottom PLT buffer layer, which may be related to the orientation [18].

Fig. 3 shows the fatigue properties of these film configurations. The measurement frequency was 5×10^4 Hz and three different levels of applied switching fields were used on each sample with the amplitudes of 1.5Ec, 3Ec, and 5Ec. In each measurement, a fresh capacitor or a fresh spot of the film was used. We also tested three points for each fatigue curve to ensure the reproducibility.

The PZT/PZT/PZT capacitors have apparent fatigue after 2×10^6 switching cycles for all three levels of applied fields, as shown in Fig. 3(a), similar to the fatigue property found in pure PZT. When the top PZT layer is replaced by the PLT layer, the PLT/PZT/PZT capacitor shows nearly fatigue-free up to 10^9 cycles under a medium driving field of 3Ec, however, its FE is not good under lower and higher fields, which can be seen in Fig. 3(b). While for the PZT/PZT/PLT capacitor, where the bottom PZT layer is replaced by PLT, fatigue-free property is obtained under a low driving field of 1.5Ec only, as shown in Fig. 3(c). When both bottom and top PLT buffer layers are used, i.e., with the film configuration of PLT/PZT/PLT, good FE can be obtained under both low and medium switching fields as shown in Fig. 3(d), but it exhibits fatigue after 10^8 cycles if the switching field is increased to 5Ec. At such a switching field, we suggest that charge injection can happen so that electrons or holes will be trapped in the interface region, which leads to interface inhibition of polarization switching.

The fatigue property of the PLT/PZT/PZT capacitor is similar to that found in SRO/PLZT capacitor by Stolichnov et al. [11], where good FE was observed under a switching field of 3Ec instead of near Ec. This character was explained by the existence of homogeneous built-in space charges throughout the film, which led to a built-in electric field (E_{bi}) across the film. If domain nucleation or switching rate for the top SRO/PLZT interface was much higher than that of the bottom PLZT/Pt interface, polarization switching was always determined by the nucleation or switching at the top interface as long as the driving electric field was greater than the sum of E_{bi} and the coercive field for the domain nucleation at the top interface. Thus, it was pointed out that the FE of the SRO/PLZT capacitor was only governed by the top interface [11]. The above mechanism, however, cannot provide satisfactory explanation to our results since the PZT/PZT/PLT capacitor shows significantly different fatigue properties from that of PLT/PZT/PZT, which has good FE under a low driving field of 1.5Ec rather than 3Ec. Based on this result, we believe that E_{bi} exists at the interfaces instead of inside the bulk because the heterostructure is only present at the interfaces. In addition, E_{bi} is different at the bottom and top PLT/Pt interfaces because the annealing process is different for the two interfaces during the fabrication. We propose that the E_{bi} value at the top Pt/PLT interface (E_{bi-top}) is much higher than that at the bottom PLT/Pt interface ($E_{bi-bottom}$), which causes different fatigue properties of the PZT/PZT/PLT and PLT/PZT/PZT structures. Obviously, E_{bi-top} and $E_{bi-bottom}$ are both existed in the PLT/PZT/PLT structure [14,15]. This may be confirmed by measuring photoinduced current, since such uncompensated built-in electric filed can lead to short-circuit current when electrons and holes are excited through a light irradiation.

In addition, the effect of the orientation on the fatigue cannot be neglected here. Liang and Wu [18] had reported that, the fatigue properties of 1 1 0) and (1 1 1)-oriented PZT films were better than that of (0 0 1)-oriented PZT film, while the (1 1 0) one had a little higher fatigue rate than the (1 1 1) one. Our results are also consistent with this conclusion. From Fig. 3(b) and (d), the fatigue property of (1 1 1)-oriented PZT film was better than that of (1 1 0)-oriented PZT film under 5Ec fields. The similar phenomenon can be found under 1.5Ec fields in Fig. 3(a) and (c).

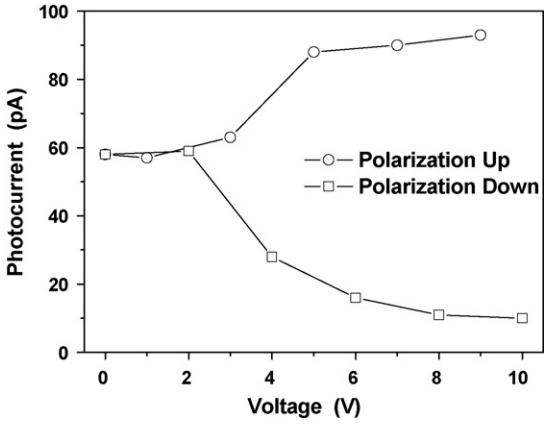

Fig. 4. Short-circuit photocurrent (PHC) of the Pt/PLT/PZT/PLT/Pt capacitor under a UV light illumination changing with the poling voltages.

Fig. 4 presents the short-circuit photocurrent (PHC) under a UV light illumination for the sample of Pt/PLT/PZT/PLT/Pt. In addition to the unpoled case, the measured point was poled with voltages changing from 0 to 10 V at a step of 1 V, respectively. For each poling step, the voltage direction was changed. The time for the poling voltage applying on the two electrodes was 20 s, and subsequently the two electrodes were short-circuit for 300 s. Then the short-circuit photocurrent was measured from the bottom electrode. When the top electrode was negative relative to the bottom one during poling, we get a poled-up state (polarization toward top electrode).

From Fig. 4, we can get that: (1) an obvious current can be obtained when the measured point is unpoled, indicating that uncompensated built-in electric filed does exist in the metal-film-metal structure; (2) if the applied poling voltages are small, the PHC keeps almost invariable, regardless of up or down poling voltage; (3) the PHC is abruptly changed when the poling voltage is approximately 3 V (79 kV/cm), close to the coercive field of 90 kV/cm; (4) with further increasing of the poling voltage, the PHC for polarization up increases, and the one for polarization down decreases; (5) when the poling voltages are far higher than the coercive field, the PHC seems saturated.

Although the origin and mechanism of the PHC in PZT films sandwiched between metal electrodes have not been fully clarified [15], in general, they are attributed to the internal built-in field (E_{bi}) due to the metal/film interfaces and the depolarized field (E_{dp}) originated from the polarization alignment in the film [14]. We note that the current shown in Fig. 4 are positive for the unpoled case. If E_{bi-top} is larger than $E_{bi-bottom}$ and their directions are opposite, E_{bi-top} should be directed to the bottom electrode. The up-polarization alignment causes an E_{dp} directed to the bottom electrode, which is in the same direction of E_{bi-top}, resulting in an enhanced positive current. Oppositely, the down-polarization alignment will decrease the current. Thus, the PHC results are consistent with our assumption that the asymmetric E_{bi-top} and $E_{bi-bottom}$ both exist in the Pt/PLT/PZT/PLT/Pt capacitor. Note in this study only the PHC for the Pt/PLT/PZT/PLT/Pt capacitor was provided to support our assumption for explaining the fatigue properties. Detailed photoelectric properties in the different metal electrode sandwiched PLT and PZT hetero-layer structures will be our further work.

4. Conclusions

In summary, several PZT films with and without PLT buffer layers were prepared by a sol–gel method on Pt/Ti/SiO_2/Si substrates. The film configurations include: PZT/PZT/PZT, PLT/PZT/PZT, PZT/PZT/PLT, and PLT/PZT/PLT. We found that the PLT bottom buffer layer induces a (1 1 1) preferred orientation in the PZT film while the PZT bottom buffer layer (made at different processing temperature from the PZT film body) induces a (1 1 0) preferred orientation in the PZT film. The remnant polarizations of the four film structures are all about 42 $\mu C/cm^2$, which is smaller than that of pure PZT film. However, adding the top and bottom PLT buffer layers lead to the increase of the coercive field.

The fatigue properties of films containing PLT buffer layers are strongly dependent on the interface nature and the switching field level. The PLT/PZT/PZT capacitor shows nearly fatigue-free up to 10^9 cycles under a medium level applied field of 3Ec, while the PZT/PZT/PLT capacitor shows good fatigue performance only under a low applied filed of 1.5Ec. The PLT/PZT/PLT capacitor is the best, which does not show fatigue behavior up to 10^8 cycles until the driving field is increased to 5Ec. We believed that such interesting fatigue properties are related to the reduction of charge carriers by the PLT and the existence of a built-in electric field at the Pt/PLT interface, as confirmed by measuring the photoinduced current of the same metal-film-metal capacitors.

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