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Effect of polarization switching cycles on the dielectric response and Rayleigh constant in $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ thin films

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$\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ thin films with good fatigue endurance were crystallized at low temperature compatible with the current semiconductor technology. The effect of polarization switching cycles on the ferroelectric properties, dielectric response, and Rayleigh constant in thin films were systematically investigated. The results indicated that the polarization switching improves the extrinsic dielectric response and dielectric nonlinearity of these thin films because of the dielectric response of the oxygen vacancy to the applied electric field, while shows weak effect on the intrinsic dielectric and ferroelectric response. Moreover, the Rayleigh constant showed different evolutions in the films prepared at different substrate temperatures. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4864761>]

I. INTRODUCTION

Lead strontium titanate ($\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$, PST) thin film has been intensively studied as a promising candidate for applications in ferroelectric random access memories (FRAM) and frequency agile devices¹ because of its superior ferroelectric as well as dielectric performances,^{1,2} weak dependence of electrical properties on grain size,³ and low crystallized temperature.⁴ Considering that the ferroelectric films should be subjected to a large number of polarization switching cycles for the FRAM applications, the endurance against suppression of switching polarization by ac voltage cycling (fatigue) is one of the most crucial properties to characterize the performance of PST thin films.⁵ Moreover, the evolution of dielectric response with the polarization switching is another important property for the applications, which decreases dramatically in the fatigued thin films⁶ while keeps a constant value for the thin films with good fatigue endurance.⁷

Raleigh law is a useful theory to investigate the domain wall and randomly defects distribution under the sub-switching field⁶ and thus have been extensively adopted for the study of fatigue behavior of ferroelectric thin films. Unfortunately, there is a lack of sufficient investigation on the effect of switching cycles on the dielectric response and polarization before the existence of obviously fatigue behavior. It is thus the aim of this investigation to study the effect of polarization switching cycles on the dielectric response as well as physical mechanism for the correlation between them.

II. EXPERIMENTAL PROCEDURE

Highly (100)-oriented $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ thin films with a thickness of 300 nm were deposited via *in-situ* r.f.-magnetron sputtering method on LaNiO_3 (LNO) coated Si substrates⁴

with an atmosphere of pure argon and Pt electrode with a diameter of 150 μm was adopted as the top electrode. The detail parameters for the preparation of PST thin films were described elsewhere.⁴ The dielectric constant and loss tangent dependence on the electric field were tested by HP4294 (Agilent Technologies, Santa Clara, CA) LCR meter under different ac voltages ranging from 0.1 to 1 V with the frequency of 10 kHz. The electric field dependent polarization hysteresis (P - E) loops and the fatigue endurance with different polarization switching cycles were measured by an aixACCT TF Analyzer 2000 system with sine wave at a frequency of 1 kHz at room temperature.

III. RESULTS AND DISCUSSION

As a basis of subsequent analysis, the polarization hysteresis (P - E) loops of the films prepared at substrate temperatures of 300, 450, and 500 °C (denoted as PST-300, PST-450, and PST-500, respectively) are demonstrated in Fig. 1. It can be found that the residual polarization P_r and the maximum polarization P_{max} increase dramatically with increasing substrate temperature and the coercive field E_c of all the films is larger than 50 kV/cm. As reported in our previous investigation,⁴ the thin films prepared at all substrate temperatures showed perfect (100) orientation although some silicon peaks can be observed, while the crystallization quality of the thin film increased with higher temperatures. Moreover, the scanning electronic microscope (SEM) results indicated that the PST-300 was partially crystallized and the crystallization was improved with higher temperatures. The inset (a) of Fig. 1 illustrates the evolution of the normalized change of residual polarization as a function of the polarization switching cycles in PST thin films deposited at different temperatures. It can be observed that there is no obvious decrease in polarization even after 10^{10} switching cycles. Moreover, the P - E loops of PST-500 before and after the polarization switching cycles,

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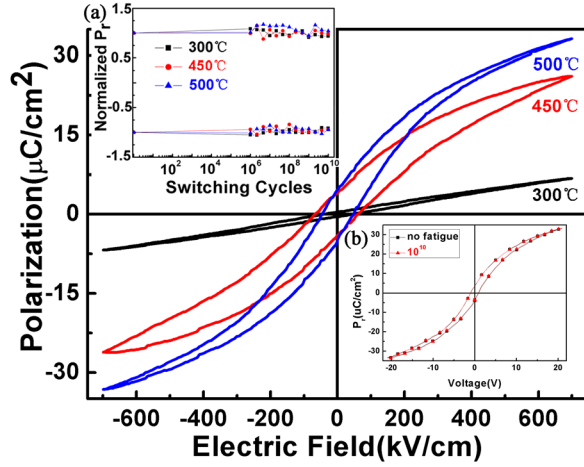


FIG. 1. P - E hysteresis loops of PST thin films *in-situ* deposited at different substrate temperatures. Insets (a) and (b) show the normalized $\pm P_r$ versus switching cycles in PST thin films prepared at different substrate temperatures and the P - E loops before and after the fatigue process in PST-500, respectively.

as demonstrated in inset (b) of Fig. 1, confirmed the good fatigue endurance of the films. While some fluctuations of the normalized polarization versus the switching cycles can be observed. This phenomenon may be attributed to the response of oxygen vacancies, formed during the pure argon deposition, to the applied electric field.⁸

The contribution of ferroelectric domain walls to the relative permittivity and the dependence of dielectric response on the strength of applied field under a sub-switching field can be expressed by Rayleigh law⁹

$$\varepsilon(E) = \varepsilon_0 \varepsilon_{init} + \varepsilon_0 \alpha E, \quad (1)$$

where the $\varepsilon(E)$ is the permittivity of the PST films under different level of applied field E , ε_{init} is the initial dielectric constant, and α is the Rayleigh constant. The samples are switched at an electric field of 100 kV/cm for a certain number of cycles via the TF Analyzer 2000 system. The dielectric constant of the PST thin films prepared at different substrate temperatures as a function of the ac electric field less than the coercive electric field before and after the polarization switching process is demonstrated in Fig. 2. The dielectric constant as a function of applied ac electric field is exhibited in parts (a)–(c) of Fig. 2 after different polarization switching cycles. Considering the derivative relationship between dielectric constant and polarization, it is strange that the dielectric response increases dramatically with larger switching cycles, while the ferroelectric response shows very weak dependence on the polarization switching cycles although some fluctuations of the normalized polarization versus the switching cycles can be observed. As reported by the previous investigations,^{10–12} the interface effect on the ferroelectric and dielectric properties is not inherent and the bulk effect is dominated factor for the thin films with LNO as bottom electrode.¹¹ Consequently, this different evolutions may be attributed to be the competition between the effect of the improved dielectric response and the bulk pinning of domain by the oxygen vacancy, both of which were mainly dominated by the bulk effect. The response of the oxygen vacancy

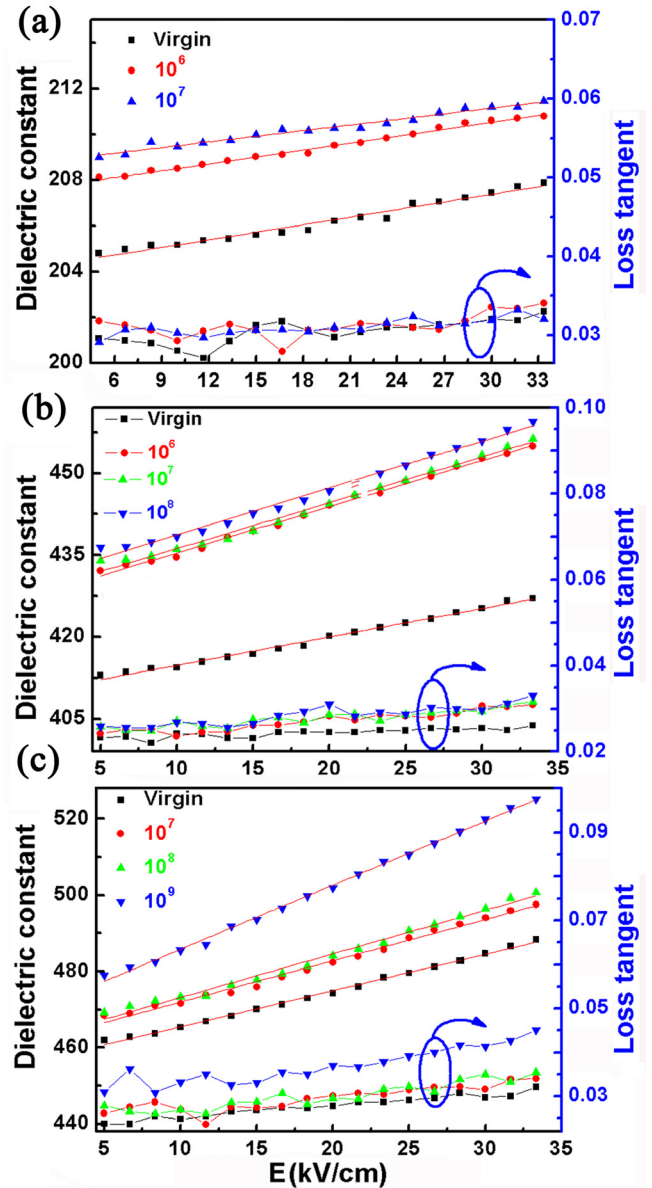


FIG. 2. The effect of switching cycles on the dielectric response and Rayleigh constant in (a) PST-300, (b) PST-450, and (c) PST-500.

with the polarization switching increases the dielectric response and hence the polarization may fluctuate. However, the migration and aggregation of oxygen vacancy on domain wall may block the switching of the domain wall and then cause the slight decreasing of polarization,^{13,14} which may be the reason for the different effects of the polarization switching on the dielectric and the ferroelectric responses. Interestingly, the dielectric response changes dramatically at less switching cycle number for the film processed at low substrate temperature, indicating the different contents of oxygen vacancy and/or the response of dielectric property to the polarization switching for the films prepared at different substrate temperatures. Moreover, as shown in Table I, the Rayleigh constant (representing the motion ability of domain wall) and the initial dielectric constant increase dramatically with the increased substrate temperature, which may be attributed the improved crystallization and motion of the

TABLE I. Effect of switching cycles on the initial dielectric constant and Rayleigh constant α in the films prepared at different substrate temperatures.

Switching cycles	300 °C		450 °C		500 °C	
	$\epsilon_r(\text{init})$	α	$\epsilon_r(\text{init})$	α	$\epsilon_r(\text{init})$	α
0	206.677	0.07431	409.61859	0.51904	456.01305	0.9496
10^6	209.828	0.0894	426.99056	0.83782
10^7	210.7215	0.09886	427.82827	0.84324	461.19911	1.08114
10^8	430.1356	0.85746	461.76927	1.14333
10^9	469.00635	1.68269

domain walls at higher substrate temperatures. Interestingly, the Rayleigh constant changes little for PST-300 because of its poor crystallization while increases dramatically for PST-450 and PST-500 with larger switching cycles.

The nonlinear dielectric property of the ferroelectric films is an important issue for the frequency agile device applications. Generally, the dielectric nonlinearity of ferroelectric materials can be obtained by adoption of the conventional Ginzburg-Landau theory.¹⁵ The dielectric tunability under an electric field E can be defined by

$$\eta = \frac{\epsilon(0)}{\epsilon(E)} = 3\beta\epsilon(0)\epsilon_0 P_{dc}^2 \approx 1 + 3\beta(\epsilon(0)\epsilon_0)^3 E^2 = 1 + KE^2, \quad (2)$$

where $\epsilon(0)$ and $\epsilon(E)$ are the dielectric constant under zero and a certain electric field, β is the coefficient of the dielectric nonlinearity. It is thus a linear relationship between $\epsilon(0)/\epsilon(E)$ and E^2 with a slope of $K = 3\beta(\epsilon(0)\epsilon_0)^3$. The nonlinear dielectric response of the thin films with different levels of crystallization was analyzed and demonstrated in Fig. 3(a). It can be observed that the tunability η increases dramatically with increasing substrate temperature because of the improved crystallization. As shown in the inset of Fig. 3(a), the coefficient of the dielectric nonlinearity decreases dramatically with increasing substrate temperature, indicating that the films prepared at low temperature is promising candidate for the frequency-agile device applications. It can be found from Fig. 3(b) that the tunability η increases dramatically with increasing polarization switching cycles because of the dielectric response of the defects with the applied electric field. The slopes of the films decrease drastically with increasing electric field because of the suppression of extrinsic dielectric response under high electric field.¹⁶ To investigate the evolution in detail, the experiment data were fitted with electric fields smaller and larger than 200 kV/cm, after which the suppression of the extrinsic dielectric response is less obvious.¹⁶ As shown in the inset of Fig. 3(b), the slope K increases gradually with higher switching cycles when the electric field is less than 200 kV/cm while changes little even under an electric field larger than 200 kV/cm, indicating that the polarization switching cycles only improve the extrinsic dielectric response while show very weak effect on the intrinsic one. Moreover, the coefficient of the dielectric nonlinearity increases a little bit under an electric field less than

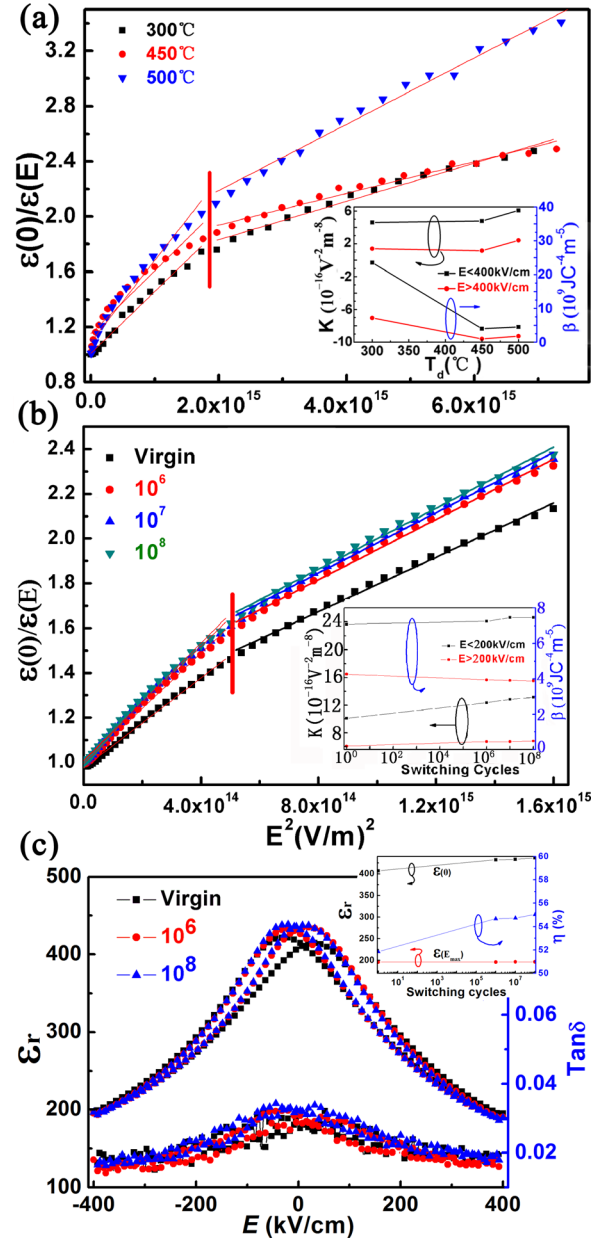


FIG. 3. Linear fits of $\epsilon(0)/\epsilon(E)$ versus E^2 for the (a) PST thin films prepared at different temperature, the (b) PST-450 with different switching cycles, and (c) the effect of switching cycles on the C-V property in PST-450. Insets in of Figs. 3(a) and 3(b) show the evolution of gradient and the coefficient of the dielectric nonlinearity with the deposition temperatures and switching cycles, respectively, the inset in Fig. 3(c) shows the dependence of dielectric constant and tunability on the switching cycles.

200 kV/cm while decreases under higher electric field with increasing switching cycles. The DC bias-field dependence of the dielectric constant of the PST-450 before and after the polarization switching process with different number of cycles is shown in Fig. 3(c), the polarization switching cycles just increases the dielectric response under zero electric field mainly owing to the response of the oxygen vacancy to the applied electric field while shows weak effect on that under the maximum electric field known as the intrinsic dielectric response mainly contributed by the lattice deformation, which is consistent with that in Fig. 3(b). As a result, the increasing of switching cycles improves the

tunability η dramatically as shown in the inset of Fig. 3(c) because of the dielectric response of the oxygen vacancy with the applied electric field. Fortunately, the slightly increased loss tangent with the increasing polarization switching cycles does not lower the properties dramatically.

IV. CONCLUSIONS

In conclusion, the effect of the polarization switching on the dielectric and ferroelectric responses in $\text{Pb}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ thin films crystallized at low temperatures was systematically investigated. The results indicated that the polarization switching improves the extrinsic dielectric response and dielectric nonlinearity for the films prepared at different temperatures, while shows weak effect on the intrinsic dielectric, ferroelectric responses, and different evolutions of Rayleigh constant with the polarization switching for the films prepared at substrate temperatures.

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