Polarization Fatigue in Ferroelectrics: Fundamentals and Recent Developments

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Abstract: In this paper, we firstly give a brief review on the fundamentals and recent developments on polarization fatigue in ferroelectric materials. The LPD-SICI model (LPD-SICI stands for local phase decomposition induced by switching-induced charge injection) developed by the present author and his colleagues has been introduced and discussed in detail. The main scenario proposed for polarization fatigue in ferroelectrics in the LPD-SICI model is that the unscreened bound charge formed at the tip of the needle-like domain at the very early stage of polarization reversal will induce an intensive charge injection (mostly electrons) near the electrode-film interface, and subsequently local Joule heating, and finally local phase decomposition around the domain nucleation site. By reviewing the recent progress on experimental studies of electrical fatigue in a variety of ferroelectric samples in both thin film and bulk form, we show that the LPD-SICI model is in good agreement with most of the observations published in the last three years in the literature. Therefore, local phase decomposition induced by switching-induced charge injection may indeed be the generic reason for polarization fatigue in a variety of ferroelectric materials, and probably antiferroelectric materials as well.

Key words: polarization fatigue; ferroelectric materials; switching; size effect; phase decomposition
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铁电材料的极化疲劳：基本机理和最新进展

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摘 要：简要回顾了铁电材料中极化疲劳现象的基本机理和最新进展。详细地介绍了作者和其合作者最近创立的 LPD-SICI 模型（LPD-SICI 是指极化翻转引起的电荷注入导致的局域相分离）。LPD-SICI 模型认为导致铁电材料中极化疲劳的主要原因是：在极化翻转早期形成的针状畴顶端的非屏蔽束缚电荷在电极－薄膜界面处会导致强烈的电荷注入（主要是电子），引起局域的焦耳热，最后在畴成核位置引发局域相分离。通过回顾过去几年在铁电材料电学极化疲劳方面实验研究的最新进展，得出 LPD-SICI 模型与过去三年中文献上发表的大多数实验观测相一致，并可以解释这些现象的起因。因此，极化翻转导致的局域相分离可能是各种类型铁电材料极化疲劳的共同起因。

关键词：极化疲劳；铁电材料；极化翻转；尺寸效应；相分离

1 Introduction

Ferroelectrics are materials which possess spontaneous polarization that can be reversibly switched by applying an external electric field. Since the discovery of ferroelectricity in Rochelle salt in the early of twenty century[1], and the subsequent discovery of barium titanate ($BaTiO_3$) in ceramic form in the middle of 1940s and lead zirconate titanate (PZT) in 1950s, there have been considerable research interest in using the materials of this kind in a variety of commercial and industrial applications, such as transducers, actuators, integrated capacitors, microwave devices, waveguides, etc. Among all these applications, ferroelectric random access memories (FeRAMs) have attracted great research attention in recent years due to their advantages over other candidates for non-volatile memory applications[2]. The advantages of FeRAMs include, but are not confined to, low operation voltage (< 5 V), high READ/WRITE speed (~ 1 ns), low power consumption, radiation hardness, and so forth[2]. However, for such memories coming to market, the problems hindering the commercialization of FeRAMs

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have to be solved properly. These problems include polarization fatigue[3-4], imprint[5-6], polarization retention loss[7-8], electric breakdown[9-11] (or time-dependent dielectric breakdown), size effect[12-14], etc.

Polarization fatigue is a systematic suppression of spontaneous polarization under bipolar (or unipolar) electric cycling. Figure 1 shows the process of polarization fatigue in a ferroelectric material. One sees that the spontaneous polarization (or switchable polarization) decreases significantly as the cycle number increases. In addition, the squareness of the hysteresis loop is lost and the loop becomes severely suppressed after repetitive electrical cycling (see the inset of Figure 1). In general, the positive and negative remanent polarization state could be encoded as the "0" and "1" state, respectively, in Boolean algebra for memory design. If the two remanent polarization states decrease below the critical point, the difference between the "0" state and the "1" state could be not detected any longer, we say that the memory element fails. Therefore, polarization fatigue is one of the most severe difficulties hindering the commercialization of FeRAMs, along with imprint and polarization retention loss[3, 15-16].

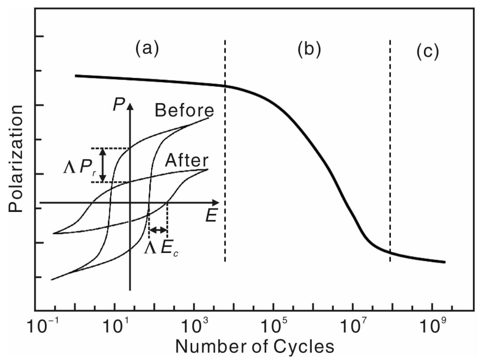

Fig. 1　Polarization fatigue in ferroelectric materials. The figure shows the decrease in spontaneous polarization as a function of electrical cycling number; the inset shows the hysteresis loop before and after polarization fatigue (after the work by Lou[3])

2　Polarization fatigue in ferroelectrics: fundamentals

In 1950s, Merz and Anderson studied the effect of bipolar electrical cycling on the polarization of $BaTiO_3$ ferroelectric single crystals[17]. They found that the spontaneous polarization of the samples decreases as switching number increases. This was the first observation of polarization fatigue in ferroelectrics in history. From then on, seen as the main obstacle holding back the full commercialization of FeRAMs, this issue has been extensively investigated both experimentally and theoretically by many researchers for more than fifty years.

During the last few decades, scientists in university laboratories and research centres have experimentally studied the effect of external and internal parameters (e. g., temperature, magnitude of electric field, frequency, doping, crystallographic orientation, electrode materials, etc.) on fatigue properties of a variety of ferroelectric materials including both thin films and ceramic/single-crystalline bulks. For more details on experimental aspects of polarization fatigue, readers are referred to a recent review article by Tagantsev et al[4] and Lou[3].

Many models and explanations for polarization fatigue in ferroelectric materials were proposed in the past. These include the domain-wall pinning model[18-22], the dead/blocking layer model[23-24], the nucleation inhibition model[4, 25], the local imprint model[26], the mechanical model[27], and the LPD-SICI model (LPD-SICI stands for the local phase decomposition induced by switching-induced charge injection)[15-16]. Again, a systematic review of the models and explanations proposed for polarization fatigue in ferroelectric materials in the past years could be found in Ref[3-4].

In Ref [3], we showed that the LPD-SICI model is in good agreement with most of the experimental observations and results in the literature. Here, let us firstly give a brief introduction about the LPD-SICI model.

Figure 2 displays a schematic diagram of polarization reversal at the earliest stage, showing that a needle-like domain has just formed from an interfacial nucleation site, and quickly propagates to the other electrode. The dark and white regions in this figure represent domains with spontaneous polarization pointing to the opposite directions. Note that the ferroelectric bound charges and the screening charges at the electrode-film interface are not drawn for better illustration. From Figure 2, we see that the head-to-head bound charges at the tip of the needle-like domain are completely unscreened, unlike those near the film-electrode interface (not drawn for simplicity). We argue that at the embryonic nucleation stage the depolarization field E_{bc} at the electrode-film interface generated by these unscreened bound charges could be extremely high (e. g., in the order of 1 ~ 10 MV/cm; $E_{bc} \sim P_r/\varepsilon_i\varepsilon_0$, where P_r is the remanent polarization, ε_i is the dielectric constant at the film-electrode interface.), especially for the situation that an interfacial "dead layer" with low dielectric constant exists, e. g. the case of Pt/PZT/Pt thin-film structures[14]. Under such a high depolarization field, we would

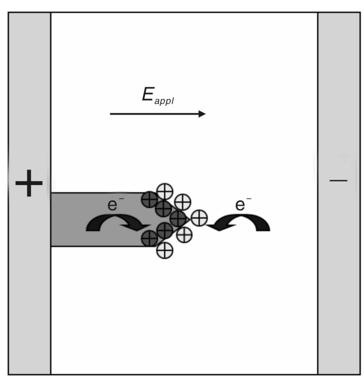

Fig. 2　The snapshot of the non-equilibrium state at an earlier polarization switching stage in a ferroelectric capacitor. Note that for better illustration the screening charges and the ferroelectric bound charges at the film-electrode interface are not drawn (after the work by Lou et al[16])

expect an extensive charge injection from the electrode to the film taking place at the domain nucleation site, which is probably determined by Fowler-Nordheim tunnelling. We believe that this process would lead to local Joule heating and subsequently local phase decomposition at the domain nucleation sites. Indeed, local phase decomposition induced by bipolar electrical fatigue was directly observed in Pt/PZT/Pt thin films by the present author and his colleagues using optical microscopy, scanning electron microscopy, and micro-Raman spectroscopy (see Figure 3a ~ c, after the work by Lou et al)[15], and later on in PZT bulk ceramics by Balk et al using scanning electron microscopy (see Figure 3d ~ f, after the work by Balk et al)[28]. The interested reader is referred to Refs [15] and [28] for more details.

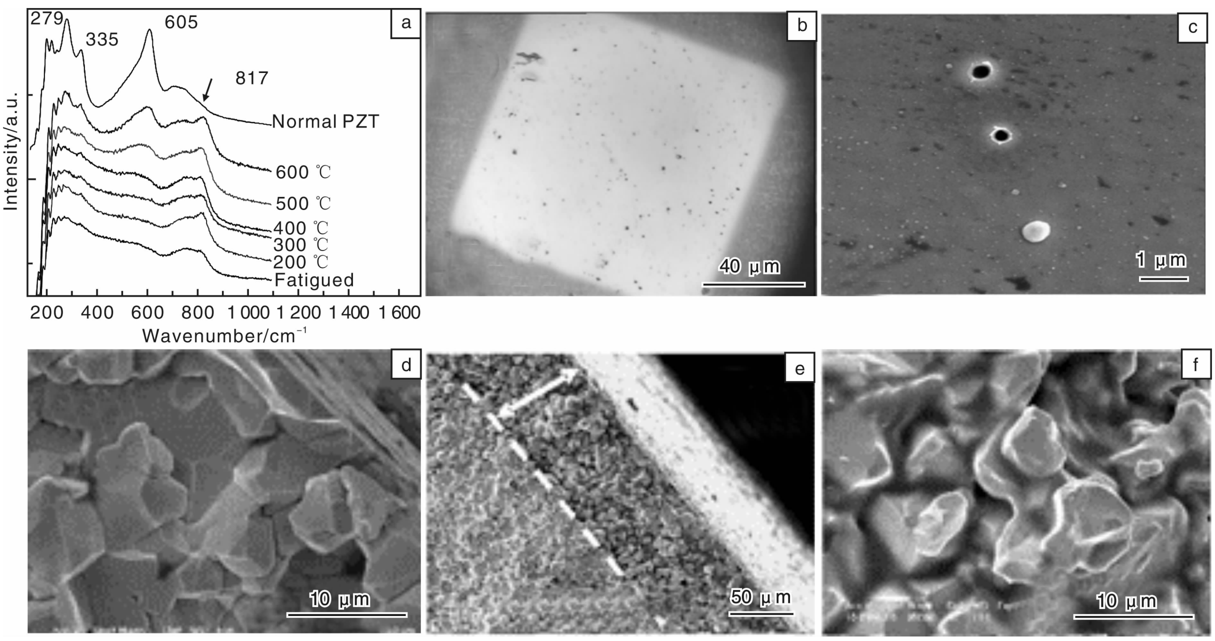

Fig. 3 (a) Raman spectra showing the restoration of the perovskite structure from a pyrochlore-like phase upon systematic furnace annealing in oxygen atmosphere (the spectrum labelled by "fatigued" was collected from the degraded region caused by local phase decomposition during fatigue process). (b) the optical image of the electrode after 10^9-cycle polarization fatigue. The dark spots on the electrode surface were due to the automatic removal of the local Pt electrode during fatigue measurements. (c) the SEM picture of two degraded spots after fatigue, indicating that local phase decomposition does occur during fatigue measurements. SEM pictures of unfatigued (d) and 3×10^5-cycle fatigued (e) ~ (f) PZT(1% La + 10.5Fe) samples. (e) and (f) are images with two different magnifications. Both show the degradation or even partial melting at the electrode-ferroelectric interface caused by local phase decomposition during electrical fatigue. ((a) ~ (c) are after the work by Lou et al.[15]; (d) ~ (f) are after the work by Balk et al[28])

We believe that local phase decomposition (LPD) could cause polarization fatigue via the following ways[3, 15-16]: ① the electric field seen by the ferroelectric part of the sample is dramatically reduced after LPD due to the low dielectric constant of the interfacial degraded layer, that is, an in-series capacitor structure forms (recall that the dielectric constant of a pyrochlorelike phase is ~40, much less than that of PZT, ~400); ② from Figure 2, we can see that the most probable places that LPD occurs are the domain nucleation sites. So the collapse of nuclei and the decrease in available nuclei number during the fatigue process makes switching more and more difficult; ③ as electrical fatigue progresses, the effective thickness of the LPD-induced interfacial degraded layer (denoted as d_i) increases with cycling number N[29]. As the depolarization field E_{dep} seen by the ferroelectric part of the film is proportional to d_i, E_{dep} would also increases with cycling number N. According to Lou theory for polarization reversal in ferroelectrics [7, 30-31], the switching retardation effect caused by the increase in E_{dep} at a later stage of polarization fatigue may be another reason for the appearance of suppressed hysteresis loops after extensive bipolar/unipolar electrical cycling.

Then, by assuming the LPD probability for one nucleation site after one cycle is $1/\lambda$ ($1/\lambda << 1$), $P_r(N)$ after N cycles is proportional to the survived nuclei number, and $1/\lambda$ is a monotonically increasing function h of the local injected power density $E_{bc}J$ around the domain nucleation site. For the simplest case in which h is a linear function, we finally obtained[16]:

$$\frac{P_r(N)}{P_r(0)} = D \cdot \exp\left\{-AN\frac{C_{FN}P_r^3}{27\varepsilon_i^3\varepsilon_0^3} \cdot \exp\left[-\frac{4\sqrt{2m^*}(q\phi_B)^{3/2}\varepsilon_i\varepsilon_0}{q\hbar P_r}\right]\right\} + F \quad (1)$$

where C_{FN} is the Fowler-Nordheim coefficient, ϕ_B is the barrier height and m^* is the electron effective mass at the interface. A is the LPD probability per unit power density per electrical cycle, $P_r(0)D$ and $P_r(0)F$ are the "fatigued" and "non-fatigued" parts of the remanent polarization, respectively, when N approaches infinity. $D + F = 1$, and D is usually much larger than F.

For more details about the LPD-SICI model and experimental evidence supporting it, readers are referred to our previous papers on polarization fatigue in ferroelectric and/or antiferroelectric materials [3, 15-16, 29, 32-33].

3 Polarization fatigue in ferroelectrics: recent developments and new experimental results

Having briefly introduced the background and fundamentals of polarization fatigue, as well as the main idea of the LPD-SICI model established by the present author and his coworkers, we now turn to some recent developments in the last three years and give a brief review on the new experimental results on this topic. In particular, we will show how the LPD-SICI model could account for these new observations.

Doping effect Recently, Karan et al reported that the fatigue properties of their PSZT films are significantly enhanced in comparison with pure PZT thin-film samples (PSZT denotes Sr doped PZT)[34]. In addition, Simoes et al found that doping 8% and 15% La into their BFO ($BiFeO_3$) films could increase the fatigue resistance of their samples in a dramatic way[35]. In both papers, a reduced remanent polarization P_r was also observed after doping. These observations are consistent with the predictions of the LPD-SICI model, which implies that the enhanced fatigue endurance may be due to a reduced remanent polarization after doping[3]. Interestingly, a suppressed hysteresis loop, an enhanced fatigue endurance and improved energy storage performance were also found for Sr-doped $PbZrO_3$ antiferroelectric thin films, in comparison with undoped $PbZrO_3$[36]. Polarization fatigue in antiferroelectrics has been studied both experimentally and theoretically by the present author and his colleagues in two recent works[32-33].

Crystallographic orientation effect Lin et al showed that fatigue in PMN-0.32PT relaxor ferroelectrics is more severe in the [111] and [110] orientations with higher remanent polarization (PMN-0.32PT stands for $Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$) while fatigue is less severe in the [001] direction with lower remanent polarization[37]. The crystallographic orientation effect or anisotropy effect on polarization fatigue has been discussed in much detail in Refs [3, 16], particularly regarding the results of Takemura et al. [38] on PZN-5.4PT single crystals. The LPD-SICI model predicts that the orientation with a higher spontaneous polarization generally gives rise to a faster fatigue rate [16]. Therefore, the results of Lin et al. are in good agreement with the predictions of our model.

Re-annealing effect Zhang and Lupascu[39] showed that although the PZT ceramics show a certain degree of recovery in terms of the squareness of hysteresis loop after a certain number of fatigue cycles and subsequent annealing process at 500 ℃ for 1 h, the refreshed film shows a much faster refatigue rate than the virgin one. These observations indicate that some permanent damages were formed after severe fatigue process and these damages could not be refreshed by re-annealing the sample at relatively low temperatures (e.g., 500 ℃). Their results are consistent with our discussion regarding the refreshment/rejuvenation of the fatigued samples using thermal re-annealing process in our previous paper[3, 15]. Furthermore, the LPD-SICI model indicates that a much higher temperature (e.g., ~1 000 ℃), comparable to the crystallization temperature of PZT ceramics, should be able to refresh the fatigued sample to its close-to-virgin state. It should be noted that re-annealing the fatigued sample and subsequent recovery of its electric properties have also been observed by other researchers[15, 40-43].

Also, Dutta et al[44] found that thermal re-annealing could rejuvenate the strain loop to some extent, while removal of the damaged surface layer under the electrode could refresh the strain to its original value. The formation of a damaged interface layer after severe polarization fatigue has been experimentally observed in our previous work using a micro-Raman spectroscopy[15]. We also showed that the degraded layer for Pt/PZT/Pt capacitors may be pyrochlore-like and has lower dielectric constant compared with that of PZT. Based on these observations, we built the LPD-SICI model for polarization fatigue in ferroelectrics. Therefore, the LPD-SICI model naturally suggests that removal of the damaged layer is an alternative way to refresh the fatigued sample to its virgin state, apart from high-T re-annealing process. Note that Verdier et al[45] also found that the remanent polarization of the fatigued PZT ceramics is almost recovered after polishing off the degraded interface layer and re-electroding the sample.

Very recently, by studying the effect of fatigue-annealing history on the electrical properties of their PZT films, Cao et al[46] showed that local phase decomposition induced by switching-induced charge injection is responsible for polarization fatigue in their PZT films. In a later paper, they pointed out that local phase decomposition during fatigue could occur not only at the interface but also in the bulk[47]. This is true. Although electron injection from the electrode can induce local phase decomposition mainly at the interface, in some cases the energetic electrons could be injected into the interior of the sample and cause phase degradation there.

Effect of electrode material and interface modification In the past, many researchers found that conductive oxide electrodes are very effective in enhancing the fatigue endurance of PZT films[3]. This phenomenon has been confirmed again recently by Han et al for PZT thick films. They showed that better fatigue properties were observed on the samples deposited on LNO/YSZ and LNO/Si substrates with LNO serving as the bottom electrode than that deposited on Pt/Si substrate (LNO denotes $LaNiO_3$; YSZ denotes yttria-stabilized zirconia)[48]. According to the LPD-SICI model[16], the use of conductive oxide electrodes could effectively eliminate the so-called interfacial "dead layer" and maintain a high bulk-like dielectric constant at the interface. This will give rise to a low E_{bc} at the film-electrode interface, and therefore low charge injection from the electrode and consequently better fatigue resistance (see Figure 2). Additionally, Liu et al showed that FePt as a top electrode is more effective in improving the fatigue resistance of their PZT thin films than Pt (see Figure 4), and they attributed this phenomenon to an interface effect and invoked the LPD-SICI model to explain their results[49].

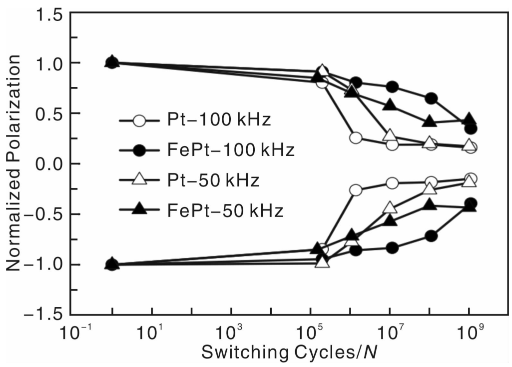

Figure. 4 Fatigue properties of FePt/PZT/Pt and Pt/PZT/Pt thin-film capacitors under 100 kHz and 50 kHz (after the work by Liu et al[49])

Electric field effect Lin et al[50] found that polarization fatigue at lower field of 1.5 kV/cm, smaller than the coercive field, is must less severe (about 20% polarization loss after 10^5 cycles) than that at higher field of 7.5 kV/cm (about 40% polarization loss after 10^5 cycles). Previously, we argue that switching is the necessary condition for polarization fatigue. Recently, we established a statistical and stochastic theory for polarization reversal in ferroelectrics [30-31]. This theory indicates that switching could also occur at a field regime that is much lower than the coercive field E_c (see Refs [7, 30-31] for more details). So the observations in this work do not contradict with our previous argument.

Changes in material properties caused by fatigue Local phase decomposition during fatigue measurements could result in the degradation of the top electrode[15]. So, we believe that the delamination of gold electrode after 10^7 fatigue cycles observed by Zhang et al [51] in P(VDF-TrFE) films is also due to the local phase decomposition and interface degradation induced by switching-induced charge injection. In addition, Luo et al [52] showed that after polarization fatigue the switching process in P(VDF-TrFE) films becomes retarded and the leakage current increases. Fatigue-induced switching retardation effect was previously observed by Verdier et al in PZT bulk ceramics [53], while higher leakage current in fatigued ferroelectric materials was reported by Scott et al [54], Wang et al [55] and Lupascu et al [56]. The consistency of these phenomena with the LPD-SICI model has been discussed in much detail in our previous paper [3].

By using quasi-static d_{33} measurements, Li et al [57] showed that fatigue is highly heterogeneous at an earlier stage, and the fatigue heterogeneity is weakened at a later fatigue stage. Similar behaviour has been reported previously [58]. Note that fatigue heterogeneity is one of the characteristics indicating that LPD-SICI may indeed be the cause of polarization fatigue.

Note that although the LPD-SICI model seems to be consistent with most of the experimental results on polarization fatigue in the literature there are still a few observations that it may confront difficulties to explain. We will give a few examples below. Also notice that though a quantitative interpretation of these phenomena using the LPD-SICI model is not available at the moment [e. g., deriving a compact equation like Eq (1)], they may be explained using a general picture of "LPD-SICI", that is, a picture of local phase decomposition induced by switching-induced charge injection, or alternatively, using a mixture of several mechanisms, e. g, the combination of the LPD-SICI scenario, oxygen vacancy or electron pinning model, and some others.

It was observed that the remanent polarization could be partially or fully refreshed in some fatigued ferroelectric thin-film capacitors via high-fatigue-number cycling [59-64] or high-field cycling [65-67]. The origin for this phenomenon is currently unknown. Researchers usually explained this behaviour using the oxygen-vacancy pinning/depinning scenario in the past. Our tentative explanations for these observations using a general picture of the LPD-SICI scenario are as follows [3]: ① a significant increase in leakage current passing through the sample caused by repetitive fatigue cycling, and/or ② the electrical breakdown or shorting of the degraded interface layer and the subsequent reincrease in the electric field seen by the ferroelectric part of the film after high-fatigue-number cycling or high-electric-field cycling.

Finally, we should point out that although the LPD-SICI model seems to be in good agreement with most of the experimental results published previously, it is very possible that the origin of polarization fatigue in ferroelectrics is a mixture of a few different mechanisms, including the LPD-SICI scenario, the oxygen vacancy/electron pinning/depinning picture, and some others. Also note that some fatigue mechanisms proposed in the literature may NOT contradict with each other. For instance, the migration of oxygen vacancies to the electrode-ferroelectric interface during repetitive electrical cycling may significantly reduce the stability of the perovskite phase against a pyrochlorelike structure, and therefore dramatically increase the probability of LPD (local phase decomposition) and consequently polarization fatigue. In this regard, more works need to be done in order to fully understand this extremely important problem that hinders many commercial applications of ferroelectric devices.

4 Conclusions

We give a brief review on the fundamentals and recent progress on the problem of polarization fatigue in ferroelectric thin films and bulk materials. Firstly, we discussed the scenarios and models proposed for polarization fatigue in the past years. Then, we introduced and give a detailed explanation about the LPD-SICI model established by the present author and his colleagues. By reviewing the recent experimental results on electrical fatigue in ferroelectric samples published in the last three years, we showed that the LPD-SICI model is in good agreement with most of the observations in the literature. Therefore, we conclude that local phase decomposition induced by switching-induced charge injection may indeed be the generic reason for causing polarization fatigue in various ferroelectrics, including both thin films and bulk materials.

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