

Imprint in PZT Capacitors: Causes and Solutions

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ABSTRACT

We show that voltage offsets in the polarization-voltage characteristics of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ capacitors can be induced by either thermal or optical processes. The thermally (optically) induced voltage shift occurs by heating (illuminating) the sample under remanence or a saturating bias. Generally speaking, the thermally-induced voltage shifts are greater than those obtained optically; this is attributed to the role of oxygen vacancy-related defect dipoles throughout the film. We find that the inclusion of a dopant element that occupies a portion of the $\text{Ti}(\text{Zr})$ sites and has an oxidation state greater than +4 reduces the thermally-induced voltage shifts observed in the capacitors.

1. Introduction

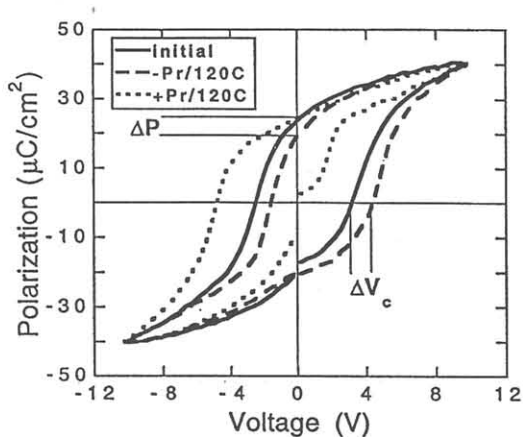
Non-volatile memories based on ferroelectric (FE) capacitors show much promise because they exhibit a spontaneous polarization that can be reversed by an electric field. One sign of the polarization can be used to store a "1", while the other sign can be used to store a "0" [1]. The realization of FE non-volatile memories is hampered to some extent because of degradation mechanisms known as fatigue and imprint. Nowadays, fatigue, which is the loss of switchable polarization with repeated polarization reversals, is better understood [2,3] of the mechanisms and can be essentially overcome by using oxide electrode materials [4]. On the other hand, imprint is significantly less understood and ill-defined. It is the purpose of this paper to better define, understand, and describe how to overcome imprint.

2. Results

Figure 1 shows the effect that occurs by heating a PZT thin film to 120°C after poling the capacitor to negative ($-P_r$) or positive ($+P_r$) remanence. These thermal processes induce a voltage shift in the P-V characteristics. The voltage shift arises from an asymmetric distribution of trapped charge [11-13]. A voltage shift of the type exhibited in Fig. 1 can lead to a memory (imprint) failure in either two ways: through either a read or a write mechanism. First, the voltage shift can lead to a reduction in the value of the polarization for one of the remanent polarization states. If the shift is large enough, the $+P_r$ and $-P_r$ states (the two logic states ("0" and "1")) may be indistinguishable during memory reading as determined by the sense amplifier. If ΔP becomes large enough, the sense amplifier may not be able to distinguish between logic "0" or logic "1", i.e., as the loops shift to the right the $+P_r$ state approaches the $-P_r$ state. (2) The second effect of the voltage shift is that the coercive voltage may become too large in one direction to be switched by the programming voltage. This case

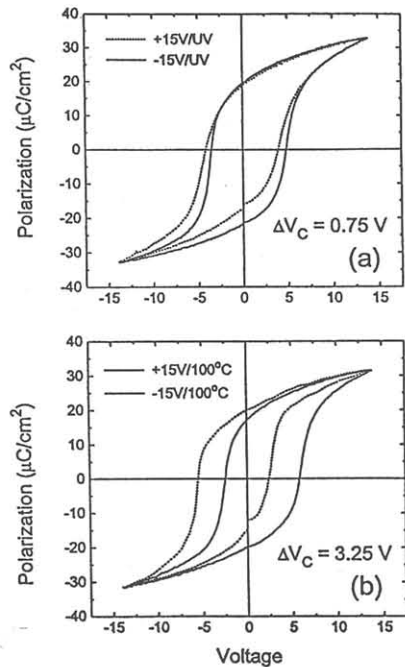
is denoted by ΔV_c in Fig. 1. When either one of these cases occur, the memory cell based on such a capacitor has failed.

Figure 1: Hysteresis loops for a PZT 30/70 film illustrating a thermally-induced voltage shift obtained by heating at $\pm P_T$ and 120°C for 2 hrs.



We show that voltage offsets in the polarization-voltage characteristics of PZT capacitors can also be induced by optically illuminating the PZT capacitor. The optically induced voltage shift occurs by illuminating the sample under remanence or a saturating bias [5]. Generally speaking, the thermally-induced voltage shifts are greater than those obtained optically. Figure 2 compares the (a) optically- and (b) thermally-induced voltage shifts at $\pm V_s$ for the same PZT 40/60 capacitor using Pt electrodes. The optical voltage shifts were induced by biasing the capacitor to $+V_s$ or $-V_s$ and then illuminating the top electrode with bandgap light.

Figure 2: (a) Hysteresis loops for a PZT 40/60 film illustrating an optically-induced voltage shift obtained by illuminating the sample at $\pm V_s$ for 30 sec. at 300 K. (b) Hysteresis loops for a PZT 40/60 film illustrating a thermally-induced voltage shift obtained by heating at $\pm V_s$ at 100°C for 24 hrs.



The larger voltage shifts obtained by the bias/heat combinations are attributed to the role of aligned defect-dipoles which will enhance the net polarization. The defect-dipole component of the polarization, P_D , is due to a volumetric distribution of aligned defect-dipole complexes in the material [6,7]. Some common defect-dipole complexes in the PZT system

might be lead vacancy-oxygen vacancy ($V_{Pb}''-V_O^{\bullet\bullet}$) complexes. Using electron paramagnetic resonance (EPR), we show that the alignment of defect-dipoles occurs upon subjecting both BaTiO₃ and PZT capacitors to a dc bias at elevated temperatures. The alignment is demonstrated to occur via orientation dependent EPR signals in the polycrystalline perovskite lattice. It is proposed that it is the net polarization that determines the spatial location of the trapped electrons; an enhanced net polarization at one electrode interface can lead to enhanced electron trapping, and thus larger voltage shifts.

Consistent with this premise, we find that the inclusion of a dopant element that occupies a portion of the Ti(Zr) sites and has an oxidation state greater than +4 reduces the thermally-induced voltage shifts observed in the capacitors. First, application of a saturating dc bias at elevated temperature leads to the largest voltage shifts. This effect likely results from the defect-dipole complexes that are more easily reoriented at elevated temperature under $\pm V_s$ than under $\pm P_r$. It may also arise in part since P_r , the driving force for the trapping, is reduced at elevated temperatures. Second, the addition of a donor dopant element that substitutes for Ti (Zr) and has an oxidation state greater than 4+ (Nb, Ta, and W) reduces the thermally-induced voltage shift (last row in Table I). We note that a seminal paper by Takahashi [8] reported on the effect of impurity doping in bulk PZT ceramics and also found that donor doping decreased the observed voltage shifts. This likely results because these particular dopants reduce the oxygen vacancy density [9] and, hence, the defect-dipole contribution to the voltage shift.

3. Conclusions

In summary, we have shown that ferroelectric materials may have the tendency to exhibit voltage shifts which we define as imprint. We have also shown similarities between thermally- and optically-induced voltage shifts. However, the thermal shifts are typically greater than those obtained optically. This difference is attributed to the role of orientatable defect-dipole complexes involving $V_O^{\bullet\bullet}$. We find that processes that tend to reduce the $V_O^{\bullet\bullet}$ concentration, such as substituting some of the Ti(Zr) sites with donor dopants lead to smaller thermally-induced voltage shifts.

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