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The Effect of Tungsten Trioxide Thin Films at Ferroelectric–Electrode Boundaries on Fatigue Behaviour

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A conventional thin film capacitor heterostructure, consisting of sol–gel deposited lead zirconium titanate (PZT) layers with sputtered platinum top and bottom electrodes, was subjected to fatiguing pulses at a variety of frequencies. The fatigue characteristics were compared to those of a similarly processed capacitor in which a ~ 20 nm tungsten trioxide layer had been deposited, using pulsed laser deposition, between the ferroelectric and upper electrode. The expectation was that, because of its ability to accommodate considerable oxygen non-stoichiometry, tungsten trioxide (WO_3) might act as an efficient sink for any oxygen vacancies flushed to the electrode–ferroelectric boundary layer during repetitive switching, and hence would improve the fatigue characteristics of the thin film capacitor. However, it was found that, in general, the addition of tungsten trioxide actually increases the rate of fatigue. It appears that any potential benefit from the WO_3 , in terms of absorbing oxygen vacancies, is far outweighed by it causing dramatically increased charge injection in the system.

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KEYWORDS: ferroelectric, thin film, fatigue, tungsten trioxide, oxygen vacancies

1. Introduction

In 1955, when Merz and Anderson¹⁾ foresaw the potential of ferroelectrics in memory applications, they were also aware of the potential problems of fatigue, the phenomenon whereby repetitive electrical cycling results in a reduction of switchable polarization.²⁾ For a ferroelectric capacitor used in a non-volatile memory cell, as the switchable polarization decreases, the switched charge also decreases to the point where it becomes difficult to distinguish between logic states, and the device ceases to function correctly. Fatigue, if present, obviously limits the lifetime and usefulness of any memory system based on ferroelectric switching. Consequently, during the relatively recent development of ferroelectric random access memory (FRAM) technology,³⁾ understanding the microscopic origin of the fatigue mechanism, and finding ways of mitigating or preventing fatigue effects became the subject of renewed interest.

The observed characteristics of fatigue vary greatly. “ ABO_3 ” perovskite ferroelectrics can suffer fatigue with elemental metallic electrodes after just 10^4 – 10^6 cycles,³⁾ but this can be radically improved by using conductive oxide electrodes such as IrO_2 ⁴⁾ (although oxide electrodes do not guarantee fatigue resistance⁵⁾) or by doping the ferroelectric with higher valence cations, such as lanthanum.⁶⁾ Some bi-layered perovskite aurivillius phases such as strontium bismuth tantalate do not fatigue readily, even with elemental metallic electrodes, up to 10^{12} cycles.⁷⁾ In addition, the fatigue process has been shown to be sensitive to the fatigue pulse profile (shape, polarity, amplitude, and period).^{8–10)}

Recent models of fatigue suggest that electrical cycling results in the creation of and/or re-distribution of defects within the ferroelectric material, causing suppression of the switchable polarization. The types of defects, how they are created or re-distributed, and the mechanisms by which they induce fatigue are important questions still open to debate. However, most research highlights oxygen vacancies as important defects, either produced in the film during deposition, or created during electric field cycling by impact

ionization from charge injection by electrons. Under field cycling, oxygen vacancies electromigrate towards the ferroelectric–electrode interface where they accumulate causing domain wall pinning.^{11,12)} It is thought that oxide electrodes improve fatigue resistance because they can absorb oxygen vacancy defects, and donate oxygen back into the ferroelectric layer. This decreases the density of point defects within the ferroelectric that are active in domain wall pinning. If this concept were correct, then one would assume that the greater the ability of an oxide to absorb oxygen vacancies, the better it would be in terms of increasing the resistance of an adjacent ferroelectric film to fatigue.

Tungsten trioxide (WO_3) is archetypal of a group of transition metal oxides, structurally somewhat similar to perovskites (composed of corner sharing ReO_6 octahedra). They are particularly noteworthy for the ease with which they can accommodate oxygen vacancies, and they might therefore be expected to be particularly effective in the inhibition of ferroelectric fatigue.¹³⁾ Importantly, oxygen-deficiency can be incorporated without introducing oxygen vacancy point defects.¹⁴⁾ Instead, a structural distortion called Crystallographic Shear (CS) accommodates local variations in oxygen content.¹⁵⁾ Matzke *et al.*¹⁶⁾ have suggested a possible sequence for forming CS planes. Initially, oxygen atoms diffuse out of the crystal leaving behind vacancy point defects which order into walls (Wadsley defects) and then shear. A series of ordered mixed-valent Magnéli phases, of the formulae $\text{W}_n\text{O}_{3n-1}$ and $\text{W}_n\text{O}_{3n-2}$, then form.¹⁷⁾

In this paper we report results from an experiment in which a thin tungsten trioxide (WO_3) layer was deposited at the interface between ferroelectric (lead zirconium titanate, PZT) and elemental metal electrode (platinum, Pt), and the fatigue characteristics investigated. Based on the suggestion that oxygen vacancies, accumulating at the ferroelectric–electrode boundary, contribute significantly to the fatigue process, it was expected that the inclusion of the WO_3 , with its particularly high efficacy for oxygen vacancy absorption, would improve fatigue characteristics by preserving full oxygenation of the interfacial ferroelectric material.

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2. Experimental Procedure

Thin film capacitors were fabricated by sol-gel spin coating onto commercial single-crystal {001} magnesium oxide (MgO) substrates on which a Pt lower electrode had been sputtered. The $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ precursor solution (0.4 M) was prepared using acetate trihydrate, zirconium propoxide and titanium butoxide as source materials, and using 2-methoxyethanol as the solvent. Ferroelectric deposition was performed by spin-coating three layers at 4000 rpm for 70 s, pyrolyzing in air on a hot plate at 300 °C for 5 min, and annealing at 600 °C for 35 min. WO_3 (when incorporated into the capacitor structure) was deposited by pulsed laser deposition (PLD) using a Lambda Physik COMPex KrF excimer laser (with $\lambda = 248$ nm), and a sintered ceramic WO_3 target. Growth parameters typically used a fluence of $\sim 2 \text{ J cm}^{-2}$, repetition rate of 10 Hz, oxygen pressure of 0.2 mbar, and substrate temperature of 600 °C. In order to complete the capacitor structure, Pt electrodes were deposited by sputtering through a shadow mask creating square upper electrodes $200 \times 200 \mu\text{m}^2$ in size. The capacitance and dielectric loss of the samples were measured by a Hewlett Packard HP4284A Precision LCR meter. A Radiant Technologies Precision Materials Analyser RS6000T Workstation was used for hysteresis, polarization and fatigue measurements.

3. Results and Discussion

Figure 1 shows a θ - 2θ X-ray diffraction (XRD) trace of a {001}-oriented WO_3 film successfully deposited directly onto a {001} MgO single crystal substrate under the growth conditions outlined above. Establishing successful growth of the thin layers of WO_3 deposited on top of the PZT films was not as straightforward through XRD, given the similarity in lattice parameters, and the small relative volume of WO_3 . Cross-sectional transmission electron microscopy (TEM) was therefore used. Figure 2(a) illustrates the form of the entire thin film capacitor structure. Energy dispersive X-ray (EDX) analysis and scanning TEM established that PLD-deposited WO_3 layers, when present, were ~ 20 nm thick [Fig. 2(b)].

The effective room temperature permittivity of the PZT was found to demonstrate limited frequency dispersion (typically $\varepsilon_{1 \text{ MHz}}/\varepsilon_{100 \text{ Hz}} \sim 0.9$), and loss tangents were consistently below 0.03. The dielectric constant of the PZT layer was calculated to be $\varepsilon \sim 250$ and the WO_3 layer $\varepsilon \sim 50$. Figure 3 shows polarization loops taken before and after 10 kHz fatigue (at 12 V) of the Pt/PZT/Pt and Pt/PZT/ WO_3 /Pt capacitors. While the pre-fatigue polarization values of the PZT without WO_3 ($\sim 40 \mu\text{C/cm}^2$) are similar to those quoted in the literature for high quality thin films,¹⁸⁾ it is clear that both samples suffer a drastic reduction in remnant polarization as a result of fatigue under relatively few cumulative switching cycles. The WO_3 layer has certainly not prevented the fatigue process. Indeed, as can be seen in Fig. 4, the addition of the WO_3 layer appears to accelerate fatigue (apart from in the 1 MHz data which did not show any fatigue, and is not plotted), completely contrary to what had been hoped, given the potential properties of the WO_3 as an oxygen vacancy sink.

Figure 5 plots the fatigue behaviour as a function of

Fig. 1. XRD (θ - 2θ) scan on a WO_3 thin film grown directly onto a {001} MgO single crystal substrate, using pulsed laser deposition. The strong peaks corresponding to diffraction maxima from {200}/(002) and {400}/(004) planes in WO_3 suggest both successful growth of the phase and strong preferential orientation.

time under electrical stress, rather than as a function of cumulative applied switching cycles, and it is through these plots that the actual role of WO_3 in determining sample fatigue can perhaps be understood. What should be noted from the plots is that for the basic Pt/PZT/Pt capacitor structure, the *time* required to cause fatigue is minimum for the 100 kHz cycling (the highest frequency at which fatigue was observed). As the switching frequency is reduced, the time needed for fatigue becomes progressively greater. This contrasts with the Pt/PZT/ WO_3 /Pt structure in that the time to fatigue appears to be almost independent of switching frequency.

Such behavioural differences can be rationalized by consideration of charge injection ideas which have, for some time, been suggested to be one of the sources responsible for fatigue,^{19–21)} through the injection-associated formation of defects local to the ferroelectric-electrode boundaries. Several ideas for charge injection have been presented in recent literature.^{22–24)} In the simplest, only charge directly injected into the film by application of an external electric field is considered. In this case, the amount of charge injected should simply be dependent on the amount of time that a capacitor has been under the externally applied field (as is the case when WO_3 is present in this work). More developed ideas include the complication of switching-induced charge injection, recently quantitatively included in fatigue modeling by Lou *et al.*,²⁴⁾ where high local fields, associated with back-switching needle domain nuclei, induce local charge injection through Fowler-Nordheim tunneling. Here, for the same amount of time under electrical stress, greater fatigue should be expected when more switching cycles have occurred, accounting qualitatively for the behaviour of the basic Pt/PZT/Pt structures without WO_3 . If the creation of charge-injection-related defects is indeed responsible for aspects of fatigue, it appears that the addition of WO_3 has altered the electronic properties of the electrode-ferroelectric interface to make direct charge injection easier, such that it completely dominates over switching-related effects. It is pertinent to note that the functional characteristics of WO_3 and reduced WO_{3-x} are rather complex—ferroelastic domain walls in reduced samples have been shown to be reasonably

Fig. 2. Cross-sectional TEM image of a typical thin film capacitor structure (a), with EDX compositional information from a line scan perpendicular to the Pt-electrodes, in a thin film capacitor in which ~ 20 nm of WO_3 has been grown between the PZT layer and upper Pt electrode (b).

Fig. 3. Hysteresis loops taken before (white circles) and after fatigue (white squares) with a stressing waveform of frequency 10 kHz and amplitude 12 V, for the basic Pt/PZT/Pt structure (a) and for the Pt/PZT/ WO_3 /Pt (b).

Fig. 4. Fatigue data for Pt/PZT/Pt (a) and Pt/PZT/ WO_3 /Pt (b) capacitors with a stress waveform voltage of 12 V. The switched polarization as a percentage of the unfatigued switched polarization is plotted against the log of the cumulative number of stressing waveform cycles in both cases.

conductive and even to superconduct at low temperature,²⁵⁾ and the pure phase has been shown to be ferroelectric over a certain temperature range.²⁶⁾ Both these features could support the notion that the WO_3 layer could enhance charge injection into the ferroelectric. Indeed, direct measurements of leakage in the capacitor structures support charge injection ideas. Figure 6 clearly shows that the room temperature leakage for capacitors with incorporated WO_3 layers is significantly greater than those without WO_3 .

4. Conclusions

The fatigue behaviour of thin film capacitors with and without the presence of an interfacial layer of WO_3 has been monitored. It has been observed that WO_3 is detrimental to the fatigue characteristics of the capacitors, in stark contrast to normal observations on the fatigue resistance offered by oxide electrodes. It appears that any potential improvement in fatigue resistance offered by absorbing oxygen vacancy

Fig. 5. Fatigue data for Pt/PZT/Pt (a) and Pt/PZT/WO₃/Pt (b) capacitors with a stress waveform voltage of 12 V. The switched polarization as a percentage of the unfatigued switched polarization is plotted against the time the stressing waveform has been applied for.

Fig. 6. Direct current leakage characteristics of Pt/PZT/Pt and Pt/PZT/WO₃/Pt capacitors (two data sets for each kind of capacitor structure) taken at room temperature. Clearly the addition of the WO₃ layer has decreased the resistivity of the capacitor structures, consistent with increased charge injection being a candidate for the accelerated fatigue observed.

defects is outweighed by the WO₃ causing a lowering of the barrier for charge injection in the system. This lowering of the interfacial barrier for charge injection is a key difference between WO₃ and other oxide layers/oxide electrodes investigated to date.

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