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Electrode contacts on ferroelectric $Pb(Zr_xTi_{1-x})O_3$ and $SrBi_2Ta_2O_9$ thin films and their influence on fatigue properties

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The degradation (fatigue) of dielectric properties of ferroelectric $Pb(Zr,Ti_{1-r})O_3$ (PZT) and SrBi₂Ta₂O₉ thin films during cycling was investigated. PZT and SrBi₂Ta₂O₉ thin films were fabricated by metalorganic decomposition and pulsed laser deposition, respectively. Samples with electrodes of platinum (Pt) and ruthenium oxide (RuO_2) were studied. The interfacial capacitance (if any) at the Pt/PZT, RuO₂/PZT, and Pt/SrBi₂Ta₂O₉ interfaces was determined from the thickness dependence of low-field dielectric permittivity (ϵ_r) measurements. It was observed that a low ϵ_r layer existed at the Pt/PZT interface but not at the RuO2/PZT and Pt/SrBi2Ta2O9 interfaces. In the case of Pt/PZT, the capacitance of this interfacial layer decreases with increasing fatigue while the ϵ_r of the bulk PZT film remains constant. This indicates that fatigue increases the interfacial layer thickness and/or decreases interfacial layer permittivity, but does not change the bulk properties. For the capacitors with RuO₂/PZT/RuO₂ and Pt/SrBi₂Ta₂O₉/Pt structures, however, the ϵ_r does not change with ferroelectric film thickness or fatigue cycling. This implies no interfacial layer exists at the interfaces and which can be correlated to the observed nonfatigue effect. Additionally, the equivalent energy-band diagrams of these different capacitor structures were proposed to complement the proposed fatigue mechanism. © 1995 American Institute of Physics.

I. INTRODUCTION

Ferroelectric thin films for use in nonvolatile memories have drawn much attention in recent years due to their bistable nature.¹⁻³ Among the many families of ferroelectrics, perovskite $Pb(Zr_xTi_{1-x})O_3$ or PZT thin films are the most extensively studied. Fatigue, retention, and imprint problems, however, limit the realization of these memories on a commercial scale. There has been great concern and interest in understanding the fatigue phenomena and in finding a fatigue free ferroelectric material for use in non-volatile memories. Some of the models that are pertinent to thin films suggest space-charge layers at the interface,⁴ accumulation of charged particles at the interface,⁵ or growth of conductive dendrites⁶ to be the cause of fatigue. Regardless of the details of the proposed mechanisms, most of the fatigue models relate the loss of polarization during reversals to the movement of point defects. Recently, Desu and Yoo⁷ have quantitatively proposed that defect entrapment at the ferroelectric-electrode interfaces, which is followed by an effective one-directional movement of defects by an internal field difference, to be the fatigue mechanism for thin-film ferroelectrics. The most obvious candidate for a mobile defect that can be trapped at ferroelectric-electrode interfaces is the oxygen vacancy, $V_{\Omega}^{,7-9}$ which has been identified as being responsible for the degradation of the leakage current (dc degradation) in capacitors based on similar materials.¹⁰ Additionally, the newly developed fatigue-free ferroelectric thin films based on a Bilayered structure, e.g., SrBi2Ta2O9 and SrBi2Nb2O9, have

been produced in many laboratories,¹¹⁻¹³ and the fatigue-free effect could be due to their low-oxygen vacancy concentrations.11

Fatigue is the decrease of switchable polarization with increased number of switching cycles. It is well known that ferroelectric PZT thin films with Pt electrodes exhibit severe fatigue problems, while less fatigue is observed for PZT thin films with oxide electrodes. It is believed that oxygen vacancies in PZT thin films can easily exchange with the oxygen in oxide electrodes, thereby reducing the oxygen vacancy pileup at interfaces and reducing the fatigue. One of the goals of this work is to provide indirect experimental evidence that is consistent with the postulation of oxygen vacancy entrapment at ferroelectric-electrode interfaces.^{7,8} Ferroelectric capacitors with Pt/PZT/Pt and RuO₂/PZT/RuO₂ structures are fabricated. Whether the oxygen vacancies accumulated at Pt/PZT and RuO2/PZT interfaces during the fatigue process is determined from the thickness dependence of low-field dielectric measurements.¹⁴ Consequently, equivalent energy-band diagrams for fresh and fatigued capacitors with Pt/PZT/Pt and RuO₂/PZT/RuO₂ structures can be proposed to complement the observed effects.

For the Bi-layered ferroelectrics, however, less oxygen vacancy concentration, $[V_0]$, could be present due to the low volatility of their oxide components, e.g., SrO, Bi₂O₃, Ta₂O₅, Nb₂O₅. The Bi-layered ferroelectric crystal (e.g., $SrBi_2Ta_2O_9$) can be considered to be a combination of a material having the formula Bi2O3 and a material having the formula SrTa₂O₆. The latter has a tungsten bronze structure by itself, but has a perovskite structure within the SrBi₂Ta₂O₉ unit cell.¹⁵ Therefore, even if the $V_0^{"}$ exist, they can be trapped in the Bi₂O₃ layers during the course of fatigue with no polarization loss. The equivalent energy-band diagram for

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 $Pt/SrBi_2Ta_2O_9/Pt$ capacitors is also proposed for comparison with the previous two proposed band diagrams.

II. EXPERIMENT

The test PZT samples chosen for this study were fabricated by metalorganic decomposition (MOD) on Pt/Ti/SiO₂/Si and RuO₂/SiO₂/Si substrates. All PZT samples had the same composition: $PbZr_{r}Ti_{1-r}O_{3}$ with x=0.53 and 10% excess PbO. Thin films were sintered in a preheated furnace at 650 °C for 30 min in an O2 atmosphere. Layered ferroelectric SrBi₂Ta₂O₉ thin films were deposited by pulsed laser deposition (PLD) onto Pt/Ti/SiO₂/Si substrates.¹¹ Films of four to six different thicknesses were fabricated and their thicknesses were determined by variable angle spectroscopic ellipsometry. Samples were then loaded in sputtering systems for deposition of top electrodes through a shadow mask. The Pt top electrodes were deposited on SrBi₂Ta₂O₉/Pt/Ti/SiO₂/Si and PZT/Pt/Ti/SiO₂/Si samples at room temperature, while the RuO₂ top electrodes were deposited PZT/RuO₂/SiO₂/Si samples at 200 °C.

Electrical measurements were done on discrete capacitors using a probe station. Low-field dielectric properties were carried out using a multifrequency LCR meter (HP-9192A) with an oscillation voltage of 50 mV and frequency of 10 kHz. The impedance spectrum analysis was performed over the frequency range of 10^2-10^5 Hz. The high-field P-E hysteresis loops were characterized on a RT66A Standardized Ferroelectric Test System. The fatigue characterization was also carried out by the RT66A in conjunction with an external signal generator, an HP-8116A pulse/function generator, with cycling frequency range of 0.5-1 MHz. Various fatigue periods were carried out from 10^1 to 10^9 cycles. Following each of the fatigue periods, low-field dielectric measurement and impedance spectrum analysis were performed.

III. RESULTS AND DISCUSSION

A. Pt/PZT/Pt

The thickness dependence of the dielectric permittivity of the capacitors with the Pt/PZT/Pt structure is illustrated in Fig. 1. The effective dielectric permittivity (ϵ_r) increases from 680 (0.11 μ m) to 1100 (0.73 μ m) in fresh samples. It is also demonstrated in Fig. 1 that ϵ_r of PZT capacitors decreases as cycling proceeds. Similar thickness dependence of ϵ_r has been reported for PMN, BaTiO₃, and PLZT thin films prepared by various techniques. The proposed mechanisms to interpret this behavior include the formation of Schottky barriers at the interfaces¹⁶ and changes in grain size or density effects.^{17,18} Recently, it has been demonstrated by Lee and Dey^{14,19} that the formation of a low ϵ_r Schottky depletion layer at the Pt/PLT contact lowers the effective ϵ_r for thin PLT films. The Schottky depletion layer exhibited a lower ϵ_r due to the dielectric saturation and piezoelectric compression.

Similar to the Pt/PLT contact, the Schottky behavior of the Pt/PZT contact has also been observed.²⁰ The equivalent energy-band diagram of a Pt/PZT/Pt capacitor is schematically illustrated in Fig. 2(a). The space-charge concentration



FIG. 1. Thickness and fatigue cycles dependence of dielectric permittivity for capacitors with Pt/PZT/Pt structure.

due to the oxygen vacancy (i.e., $[V_0]$) at the surface and the inner ferroelectric region for PZT thin films have been estimated to be 5×10^{20} and 1×10^{18} cm⁻³, respectively.²¹ Therefore, the band bending associated with Schottky contacts exhibited a higher slope near the contacts and a lower slope near the bulk of the PZT film. Note that the depletion regions extend right into the interior of the PZT thin film, a result of the high ϵ_r of the PZT, or of the total space charge being too low. Because the depletion regions do not effectively screen the interior from the surface, the energy from the lowest point of the bottom of the conduction band to the Fermi level [i.e., qV_n in Fig. 2(a)] is greater than $(q\psi_i - q\chi)$, where $q\psi_i$ and $q\chi$ are the work function and electron affinity of PZT film, respectively.

According to Fig. 2(a), the measured capacitance (C_m) of Pt/PZT/Pt capacitor is composed of three capacitors in series: a capacitor representing the bulk material (C_B) and two representing the interfaces (C_i) . The capacitance value of the sample can be formulated as follows:



FIG. 2. Proposed energy-band diagrams of capacitors with Pt/PZT/Pt structure at states of (a) fresh and (b) after fatigue. The dash line in (b) is for the same capacitor with fresh state.



FIG. 3. The fatigue cycle and thickness dependence of $1/C_m$ for Pt/PZT/Pt capacitors. The parallel lines indicate that the ϵ_B does not change with fatigue cycles.

$$\frac{1}{C_m} = \frac{1}{C_B} + \frac{2}{C_i},$$
 (1)

$$\frac{d_m}{\epsilon_r \epsilon_0 A} = \frac{d_B}{\epsilon_B \epsilon_0 A} + \frac{2d_i}{\epsilon_i \epsilon_0 A},\tag{2}$$

where d_m and ϵ_r are total sample thickness and dielectric constant respectively; d_B and ϵ_B are bulk thickness and dielectric constant respectively; d_i and ϵ_i are interfacial layer thickness and dielectric constant respectively; ϵ_0 is the permittivity of free space; and A is the sample area. The interfacial layer thickness (d_i) has been estimated to be ~200 Å, ^{19,22} which is much smaller than the film thickness (d_m) . Therefore, $d_B \approx d_m$, and Eq. (2) can be approximated by

$$\frac{1}{C_m} = \frac{d_m}{\epsilon_B \epsilon_0 A} + \frac{2}{C_i}.$$
(3)

Thus, a plot of $1/C_m$ vs d_m yields $1/C_i$ from the y-axis intercept and bulk thin-film permittivity ϵ_B from the slope. Figure 3 illustrates such plots for capacitors with different fatigue periods along with their corresponding ϵ_B . Note that if d_i was known and $1/C_m$ vs d_B were plotted, the slopes of these plots should be same as in Fig. 3. Hence, Fig. 3 can distinguish the factors of interfacial capacitance (C_i) and bulk dielectric constant (ϵ_B) for each period of fatigue periods implied that ϵ_B was constant and C_i was decreasing as the fatigue progressed. By rearranging the data, Fig. 4 illustrated the change ratio of ϵ_B and C_i along the fatigue periods. In summary, more capacitor fatigue resulted in a wider depletion width and/or a smaller dielectric permittivity at the interface but the bulk dielectric permittivity remained constant.

A quantitative fatigue mechanism has been developed by Desu and Yoo⁷ based on defect entrapment at ferroelectricelectrode interfaces. These defects can drift to interfaces due to the resultant internal field difference. The most probable candidate for the mobile defect is the oxygen vacancy



FIG. 4. The change ratios of C_i and ϵ_B on Pt/PZT/Pt capacitors after various fatigue periods.

 (V_0) . Note that the oxygen vacancy concentration for the fatigued PZT capacitor could be higher than that of the fresh sample, and that the mechanism for the generation of V_{0} was proposed by Mihara et al.22 Interestingly, the observed data (ϵ_B constant, C_i decreasing) in this study also indicates that a higher concentration of V_0 was introduced at the Pt/PZT interfaces as the fatigue progressed. The equivalent energyband diagram for the fatigued PZT capacitors with the structure Pt/PZT/Pt can then be represented as in Fig. 2(b). The higher concentration and higher total amount of V_{Ω} induce a deeper band bending and a higher effective interfacial layer thickness (d_i) , respectively, at the Pt/PZT interfaces. The former results in a higher interfacial electric field and consequently a lower ϵ_r at the interfaces. These two effects (i.e., low ϵ_r and high d_i) keep lowering the interfacial capacitance (C_i) and effective ϵ_r of the PZT capacitor as the fatigue progresses. Note that the internal electric field [i.e., slope of the conduction band in Fig. 2(b)] in the bulk PZT thin film is diminished as the $V_{0}^{"}$ moves toward the interfaces, explaining the slight increase in ϵ_B with increasing fatigue period (Fig. 4).

The P-E hysteresis loops for a Pt/PZT/Pt capacitor measured under various conditions are shown in Fig. 5. A symmetric P-E hysteresis loop with $P_r \sim 21 \ \mu C/cm^2$ and $E_c \sim 37$ kV/cm was observed in the fresh PZT capacitor with an applied voltage of 5 V (loop A in Fig. 5). This capacitor was then subjected to a fatigue test (± 5 V, 1 MHz) with 4×10^7 cycles which yielded a diminished P_r (loop B in Fig. 5). The P_r of the fatigued capacitor, however, can be regained with an applied voltage of 14 V (loop C in Fig. 5). This experiment indicates that domains within the bulk of a fatigued PZT thin film can be activated by a higher applied voltage. Alternatively, the physical properties of the bulk of PZT thin film are not altered by the fatigue cycling. The lowering of P_r at lower applied voltages of the fatigued capacitor could be due to either domains locked by the surface space charges or a smaller fraction of the applied voltage seen by the bulk of PZT thin films. This result is consistent with the unchanged ϵ_B for fatigued capacitors.

Furthermore, we can represent the PZT capacitor as an equivalent RC circuit shown in the closed caption of Fig. 6.



FIG. 5. The P-E hysteresis loops for a Pt/PZT/Pt capacitor measured under various conditions. Loop A: fresh capacitor with an applied voltage of 5 V. Loop B: fatigued capacitor with an applied voltage of 5 V. Loop C: fatigued capacitor with an applied voltage of 14 V.

By using impedance spectroscopic techniques, different RC components in the equivalent circuit of any dielectric medium can be separately identified. The total impedance of a simple RC circuit can be expressed as Z=R-jX. The resistance (R) and reactance (X) of the impedance (Z) for this equivalent RC circuit can be derived from following equations:

$$R = \frac{2R_i}{1 + \omega^2 R_i^2 C_i^2} + \frac{R_B}{1 + \omega^2 R_B^2 C_B^2},$$
 (4a)

$$X = \frac{2\omega R_i^2 C_i}{1 + \omega^2 R_i^2 C_i^2} + \frac{\omega R_B^2 C_B}{1 + \omega^2 R_B^2 C_B^2},$$
(4b)

where R_i and R_B are the resistance of interfacial layer and bulk, respectively; and ω is the applied frequency. Note that the reactance X also equals $(-1/\omega C_m)$. Therefore, the effects of the various RC components can be separately identified by looking at the low-frequency peaks in the impedance spectra (plotting -X vs ω) if the various C's have significantly different values from one another.

The impedance spectrum of the fatigued Pt/PZT/Pt capacitor is illustrated in Fig. 6. The impedance spectrum re-



FIG. 6. Impedance spectrums of the Pt/PZT/Pt capacitor after various fatigue periods.



FIG. 7. (a) Thickness and (b) fatigue-cycle independence of ϵ_r on RuO₂/PZT/RuO₂ capacitors.

vealed low-frequency peaks which were beyond the scope of the analyzer. These peaks were the effects of RC resonance at the interface of Pt/PZT, since we assumed that C_B had a significantly lower value compared with C_i in Eq. (4). As the fatigue cycles progressed, the resonance frequencies gradually increased (right shifted) due to the reduction of the RCconstant at the interface. Although the shift implied the reduction of either C_i or R_i , it was consistent with the above discussion that C_i decreased gradually with fatigue due to the increasing of depletion-layer thickness and decreasing of depletion-layer permittivity.

B. RuO₂/PZT/RuO₂

For the capacitor with the structure RuO₂/PZT/RuO₂, however, values of ϵ_r are essentially constant (~1200) for different capacitor thicknesses [Fig. 7(a)]. Note that the ϵ_B of the Pt/PZT/Pt capacitor presented in Fig. 4 is also ~1200. Additionally, ϵ_r of RuO₂/PZT/RuO₂ capacitors does not degrade with increasing fatigue cycles [Fig. 7(b)]. These observations imply that there is no interfacial layer between RuO₂ and PZT. The absence of depletion layers at RuO₂/PZT interfaces and the ability of RuO₂ electrodes to consume V_O by increasing their nonstoichiometry prevent the accumulation of V_O at RuO₂/PZT interfaces during fatigue cycling.

The equivalent energy-band diagram of a capacitor with the RuO₂/PZT/RuO₂ structure is illustrated in Fig. 8(a). Since the contact between RuO₂ and PZT is of the Schottky type,²³ band bending should be observed at the two interfaces. The Schottky barrier height $(q \phi_{Bn})$ at the RuO₂/PZT contact, however, is much lower than that at the Pt/PZT contact. Therefore, the depletion regions are very short and can effectively screen the interior from the surface. The effect of

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FIG. 8. Proposed energy-band diagrams of capacitors with (a) $RuO_2/PZT/RuO_2$, and (b) $Pt/SrBi_2Ta_2O_2/Pt$ structures.

interfacial capacitance on the total effective capacitance is diminished in this case due to small depletion layer thickness and high interfacial capacitance. The commonly observed high leakage currents associated with $RuO_2/PZT/RuO_2$ capacitors can also be explained by the low Schottky barrier heights.

C. Pt/SrBi₂Ta₂O₉/Pt

Similar to the previous case, a relatively constant ϵ_r was observed for various thicknesses of capacitors with the Pt/SrBi₂Ta₂O₉/Pt structure [Fig. 9(a)]. The ϵ_r of Pt/SrBi₂Ta₂O₉/Pt capacitors also does not degrade with increasing fatigue cycles [Fig. 9(b)]. These two effects clearly indicate that V_0 do not accumulate at Pt/SrBi₂Ta₂O₉ interfaces during fatigue cycling. This could be due to the inherently low defect (V_0) concentration of the SrBi₂Ta₂O₉ crystal structure and that the Bi₂O₃ layers in the layered crystal



FIG. 9. (a) Thickness and (b) fatigue-cycle independence of ϵ_r on Pt/SrBi₂Ta₂O₉/Pt capacitors.

structure block the V_0 from propagation during the course of fatigue. The equivalent energy-band diagram is then proposed in Fig. 8(b). Band bending is not observed at the Pt/SrBi₂Ta₂O₉ Schottky contact due to the low defect concentration of the SrBi₂Ta₂O₉. Therefore, no high-field induced low- ϵ_r interfacial layer was observed and the thickness independence of ϵ_r can be demonstrated.

IV. CONCLUSIONS

It was found that a low ϵ_r layer exists at the Pt/PZT interface but not at the RuO2/PZT or Pt/SrBi2Ta2O9 interfaces. The low ϵ_r layer at the Pt/PZT interface is the Schottky depletion layer where dielectric saturation and piezoelectric compression occur as a result of the strong electric field. The capacitance of this Schottky depletion layer decreases as fatigue proceeds while the ϵ_r of the bulk of the PZT film remains constant. This suggests that fatigue increases the interfacial layer thickness and decreases the interfacial layer permittivity, but does not change the bulk properties. The observed data may indicate that oxygen vacancies pile up at the Pt/PZT interfaces. For the capacitors with a RuO₂/PZT/RuO₂ or Pt/SrBi₂Ta₂O₉/Pt structure, the ϵ_r did not change with thickness or fatigue. This may indicate that oxygen vacancies do not pile up at these interfaces and, therefore, no significant fatigue was observed. The energyband diagrams of these three different capacitor structures were proposed to complement the proposed fatigue mechanism.

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