

論文 / 著書情報
Article / Book Information

Title	Leakage behavior of DC electrically degraded (Ba,Sr)TiO ₃ thin films
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Journal/Book name	IEEE Trans. Device Mater. Reliab., vol. 4, , p. 268
発行日 / Issue date	2004, 6
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Leakage Behavior of DC Electrically Degraded (Ba, Sr)TiO₃ Thin Films

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Abstract—The phenomena of dc electrical degradation of (Ba_{0.5}Sr_{0.5})TiO₃ thin films was studied. From our experimental and analytical results of current versus voltage (*I*-*V*) characteristics, it was shown that the degraded devices exhibited analogous leakage behaviors with the devices which have thin intercalated (Ba_{0.5}Sr_{0.5})TiO₃ layers with intentionally introduced oxygen vacancies between cathodes and thick (Ba_{0.5}Sr_{0.5})TiO₃ layers without intentionally introduced oxygen vacancies. This could be explained by assuming that oxygen vacancies accumulate at the interfaces between the cathodes and the (Ba_{0.5}Sr_{0.5})TiO₃ films after fatigue.

Index Terms—(Ba, Sr)TiO₃, degradation, interface, oxygen vacancy, thin film.

I. INTRODUCTION

CORRESPONDING to the overwhelming demand for devices with higher speeds and smaller sizes, materials with very large dielectric constants and low losses at microwave and millimeter-wave frequencies are becoming increasingly important. (Ba_{0.5}Sr_{0.5})TiO₃ thin-film capacitors are candidates for high-speed dynamic random-access memories, tunable devices of millimeter-wave applications, decoupling devices for high-speed CPUs, and so on.

In this work, we studied dc electrical degradation of (Ba_{0.5}Sr_{0.5})TiO₃ thin films. High electric fields are produced in thin films even at low applied voltages. Therefore, dielectric degradation is a serious problem. In the case of ceramics having the perovskite structure, it is hypothesized that positively charged oxygen vacancies are transported toward the cathode while constant-voltage stress is applied to metal-insulator-metal (MIM) capacitors, and that the degradation of ceramics having the perovskite structure can be attributed to the accumulation of oxygen vacancies at the interface between the cathode and the dielectric [1]–[3]. It has been reported that the current versus voltage (*I*-*V*) characteristics of thin films having the perovskite structure are affected by oxygen vacancies [4]–[10]. The *I*-*V* characteristics of (Ba_{0.5}Sr_{0.5})TiO₃ thin films abide by the Schottky emission model in a low-electric-field region, and by the Poole-Frenkel model in a high-electric-field region [7]. Furthermore, it was confirmed that the applied electric field boundary for the virgin device between the Schottky emission region and the Poole-Frenkel region shifted to a higher electric field as the O₂/(Ar + O₂) mixing ratio (OMR) during sputtering increased, due to the compensation of oxygen vacancies [9].

It is assumed that the accumulation of oxygen vacancies at the interface between the cathode and the dielectric after fatigue affects the width of the depletion layer. Therefore, we examined the *I*-*V* characteristics of (Ba_{0.5}Sr_{0.5})TiO₃ thin films in the relatively low electric-field region [from 23 kV · cm⁻¹ to 930 kV · cm⁻¹ in the positively biased region in which electrons are injected from the bottom electrodes (Pt) with relatively high work function to the (Ba_{0.5}Sr_{0.5})TiO₃ films, from 23 kV · cm⁻¹ to 230 kV · cm⁻¹ in the negatively biased region in which electrons are injected from the top electrodes (Au) with relatively low work function to the (Ba_{0.5}Sr_{0.5})TiO₃ films] before and after a fatigue test. The fatigue test was run under the dc voltage stress of 4 V at 418 K. The reason that voltage of 4 V was applied is that the device is expected to be used for decoupling of CPUs with 3.3-V power source lines.

II. EXPERIMENTAL

Fig. 1(a) shows a cross-sectional configuration of the test capacitor used for electrical measurements. Fig. 1(b) shows an overview of the test capacitor (passivation films are stripped). Table I shows physical attributes of the test capacitor used for electrical measurements. The fabricated capacitors have ball grid array (BGA) terminals which consist of Sn-Ag-Cu-based solder. Each ball exists on a 1-μm-thick Ni ball-limiting-metal (BLM) layer. The 50-nm-thick Pt bottom electrodes (the cathode) were deposited on the TiO₂-coated sapphire substrates with a thickness of 250 μm by dc sputtering. Physical Ar etching was used to pattern them in an electron cyclotron resonance plasma etcher. The 430-nm-thick (Ba_{0.5}Sr_{0.5})TiO₃ films of (Ba_{0.5}Sr_{0.5})TiO₃ were deposited on the bottom electrodes by RF magnetron sputtering at a fixed power density of 3.1 W · cm⁻² with a (Ba_{0.5}Sr_{0.5})TiO₃ target. 72 sccm of Ar and 18 sccm of O₂ were introduced in the chamber during the deposition of (Ba_{0.5}Sr_{0.5})TiO₃ films. O₂/(Ar + O₂) mixing ratio (OMR) is 20%. Substrate temperature was kept at 640 °C during the deposition of (Ba_{0.5}Sr_{0.5})TiO₃ films. The (Ba_{0.5}Sr_{0.5})TiO₃ films were patterned using the wet etchant of HNO₃-HF-H₂O solution. The 300-nm-thick Au top electrodes (the anode) were deposited on the (Ba_{0.5}Sr_{0.5})TiO₃ films by dc sputtering and then patterned using the wet etchant of KCN-H₂O solution. A 2-μm-thick silica passivation films were deposited on the top electrodes by chemical vapor deposition. The silica passivation films were patterned by reactive ion etching with O₂ and CF₄. Finally, a 3-μm-thick polybenzocyclobutene (BCB) films were spin-coated onto the silica passivation films and patterned by wet lithography. The obtained thin film capacitors were mounted on an evaluation board with BGA attachments, and a fatigue test was

Manuscript received November 26, 2004; revised March 2, 2004.

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Digital Object Identifier 10.1109/TDMR.2004.827270

TABLE I
PHYSICAL ATTRIBUTES OF THE TEST CAPACITOR USED FOR ELECTRICAL MEASUREMENTS

Top Electrode:	Au
Dielectric:	(Ba _{0.5} Sr _{0.5})TiO ₃
Thickness of (Ba _{0.5} Sr _{0.5})TiO ₃ :	
Virgin & Degraded:	430 nm
with intentionally introduced oxygen vacancies:	
	400 nm (OMR=20%) + 30 nm (OMR=3.3%) = 430 nm
Bottom Electrode:	Pt
Area of Capacitor:	2.8 mm ²
Capacitance:	34.1 nF (Virgin)
	33.7 (Degraded)
	30.9 (with intentionally introduced oxygen vacancies)

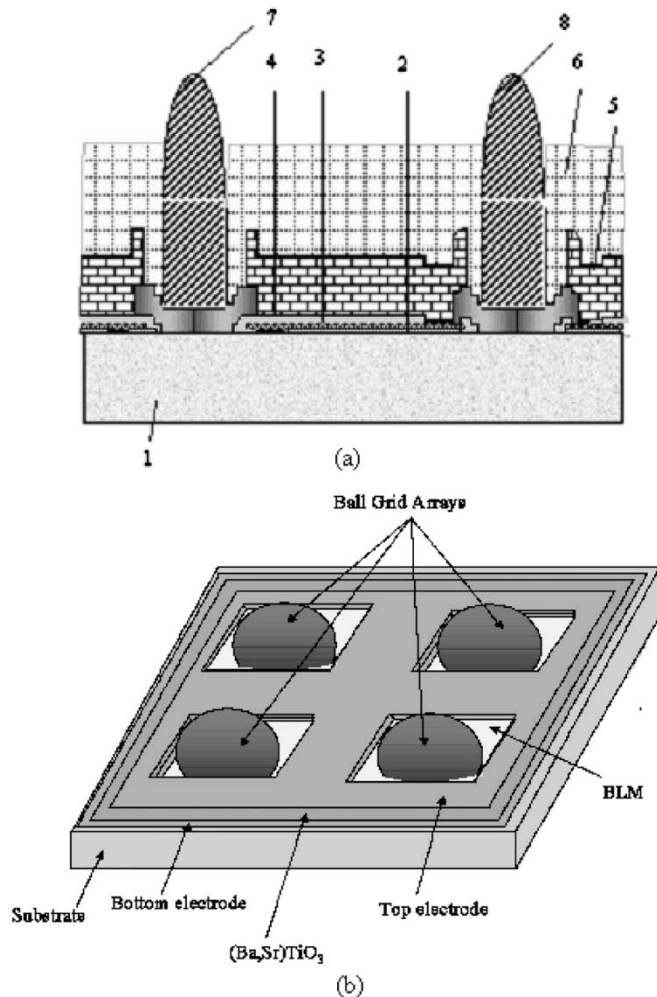


Fig. 1. A schematic diagram of the test capacitor used for electrical measurements. [1: substrate, 2: cathode, 3: (Ba_{0.5}Sr_{0.5})TiO₃, 4: anode, 5: silica passivation film, 6: BCB passivation film, 7, 8: ball grid array terminals.] The area of (Ba_{0.5}Sr_{0.5})TiO₃ thin film is 2.8 mm².

run under the dc voltage stress of 4 V¹ at 418 K (the maximum temperature for using our epoxy-resin-based evaluation board)

¹An electric field of 93 kV · cm⁻¹ was applied across the (Ba_{0.5}Sr_{0.5})TiO₃ films.

for 400 h. The life for the device used at 333 K (60 °C) becomes 360 times of the life for the device used at 418 K (145 °C), when we allow for a 2× degradation in speed for a 10 K rise in temperature. This assumption is reasonable because the activation energy obtained from the ratio between the mean-time-between-failure (MTBF) of 1310 h under a fatigue test at 398 K and the MTBF of 412 h under a fatigue test at 418 K was 0.83 eV (this data is not shown in this paper). In the present studies, the activation energy obtained for oxygen vacancy motion in pulsed laser deposited (Ba_{0.5}Sr_{0.5})TiO₃ films was around 1 eV [13], [14]. The life of 400 h at 418 K becomes more than 16 year's life at 333 K (60 °C). The end-of-life tolerable leakage current is specified at 1 μA. A dc-bias voltage was applied to the top electrodes during the fatigue test. Before and after the fatigue test, the *I-V* characteristics were measured using a HP4145 B pA-meter. The direct current bias took the form of stepwise voltage ramps, and then a leakage current was measured at each step. The height of each step was 1 V, delay time was 60 s, and retention time after the delay time, including measurement time, was 1 s. The dc-bias voltage was applied to the top electrode.

To verify the degradation mechanism, we prepared the devices which have thin intercalated (Ba_{0.5}Sr_{0.5})TiO₃ layers with a thickness of 30 nm prepared at low OMR of 3.3% between the bottom electrodes and thick (Ba_{0.5}Sr_{0.5})TiO₃ layers with a thickness of 400 nm prepared at high OMR of 20%, and their examined *I-V* characteristics before fatigue. The 30-nm-thick (Ba_{0.5}Sr_{0.5})TiO₃ films with intentionally introduced oxygen vacancies was deposited on the bottom electrodes at 3.3% OMR, and the 400-nm-thick (Ba_{0.5}Sr_{0.5})TiO₃ films without intentionally introduced oxygen vacancies were deposited on the 3.3% OMR films at 20% OMR, and the total thickness of (Ba_{0.5}Sr_{0.5})TiO₃ films was 430 nm.

III. RESULTS AND DISCUSSION

The Schottky emission model is represented by [8]

$$\ln(J_{SE}) = \ln(A^*T^2) - \frac{e^*\phi_B}{kT} + \frac{\beta_{SE} \left(\frac{ne^*N_{SC}V}{\epsilon_i\epsilon_0} \right)^{\frac{1}{4}}}{kT} \quad (1)$$

$$\beta_{SE} = \left(\frac{e^*3}{4\pi\epsilon_d\epsilon_0} \right)^{\frac{1}{2}} \quad (2)$$

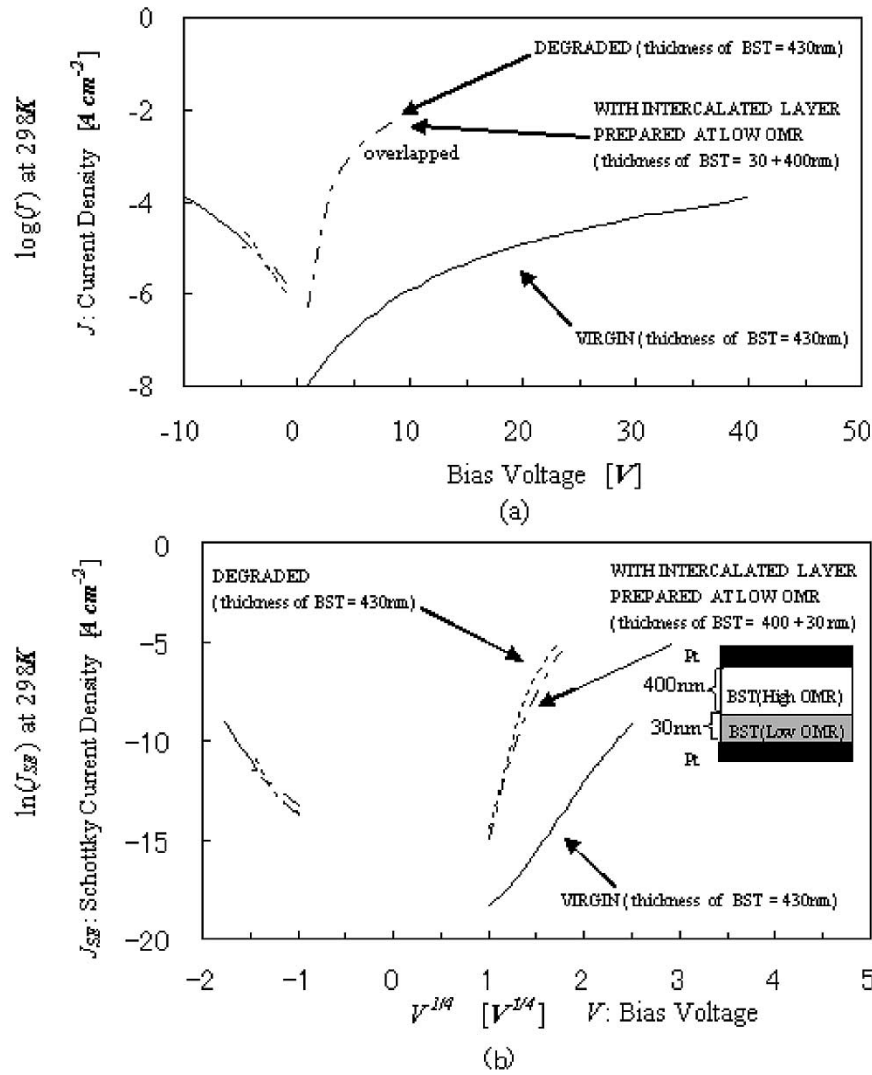


Fig. 2. (a) Plot of current density (J) at 25 °C versus V of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films. (b) Plot of $\ln(J_{SE})$ at 25 °C versus $V^{1/4}$ of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films.

where J_{SE} is the Schottky current density, A^* is a constant which can be given by $4\pi m^* e^* k^2 / h^3$ with m^* being the effective mass of an electron, e^* the effective charge of an electron, k Boltzmann's constant and h Planck's constant. T is the absolute temperature, ϕ_B is the barrier height, ϵ_d is the dynamic dielectric constant, and ϵ_0 is the dielectric constant of free space. N_{SC} is the positive space-charge density in the dielectric, because we consider that the positive space-charge is attributed to oxygen vacancy, $n = 4$. V is the applied voltage across the dielectric, and ϵ_i is the dielectric constant of the interface layer. This model describes the injection of electrons from the cathode to the dielectric in the depletion region between the cathode and the dielectric, where the Schottky emission occurs.

Fig. 2(a) shows the plot of our experimental results for current density (J) at 25 °C versus V of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films. Fig. 2(b) shows our analytical results obtained using (1) and (2) as $\ln(J_{SE})$ at 25 °C plotted versus $V^{1/4}$ of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films.

As shown in Fig. 2(a) and (b), the leakage current of the degraded device increases more than that of the virgin device in the positively biased region (electrons are injected from the bottom

electrodes to the $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ films). However, the leakage current of the degraded device is comparable with that of the virgin device in the negatively biased region (electrons are injected from the top electrodes to the $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ films).

As shown in Fig. 2(b), the slopes are given by

$$\text{slope} = \frac{1}{KT} \left(\frac{e^* N_{SC}}{4\pi^2 \epsilon_d^2 \epsilon_i^4} \right)^{\frac{1}{4}}. \quad (3)$$

The slope of the degraded device in the positively biased region is steeper than that of the virgin device, as shown in Fig. 2. Therefore, it is concluded that N_{SC} at the interface between the bottom electrode (the cathode) and the $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ film of the degraded device is higher than that of the virgin device, and/or ϵ_d at the interface between the bottom electrode (the cathode) and the $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ film of the former is lower than that of the latter, and/or ϵ_i at the interface between the bottom electrode (the cathode) and the $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ film of the former is lower than that of the latter. The acceleration of the injection of electrons driven by the local electric field generated by the oxygen vacancies accumulated at the interface after

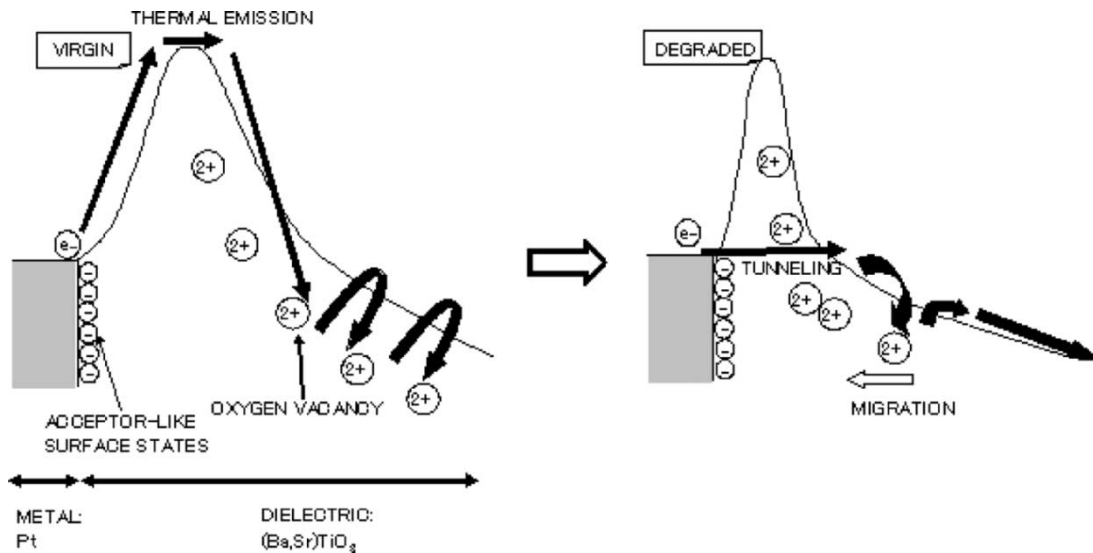


Fig. 3. Schematic energy-band diagrams accounting for the mechanism of dc electrical degradation of (Ba_{0.5}Sr_{0.5})TiO₃ thin films. Oxygen vacancies near the interface compensate for the negative charges of the acceptor-like surface states [11]. For the degraded device, the width of the depletion layer decreases, probably due to the accumulation of oxygen vacancies at the interface [12].

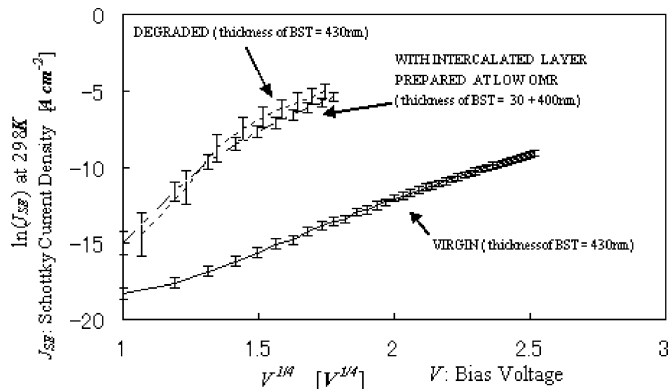


Fig. 4. Plot of $\ln(J_{SE})$ at 25 °C versus $V^{1/4}$ of the virgin devices ($n = 10$). The top and bottom limits of $\pm 3\sigma$ are indicated in the figure.

fatigue. The acceleration of the injection of electrons lowers ε_d . Therefore, higher N_{SC} and lower ε_d for the degraded device are reasonable. The oscillation of the oxygen vacancy occurs only at a low frequency on the μHz order. Because the accumulation of oxygen vacancies causes ε_i to become high, it is conceivable that ε_i does not steepen the slope. We confirmed that the relative dielectric constant for (Ba_{0.5}Sr_{0.5})TiO₃ thin films at 1 kHz was 890 before and after fatigue. However, we could not obtain ε_i experimentally.

It is assumed that oxygen vacancies near the interface between the cathodes and the (Ba_{0.5}Sr_{0.5})TiO₃ films compensate for the negative charges of the acceptor-like surface states [11]. For the degraded device, the width of the depletion layer is assumed to decrease due to the accumulation of oxygen vacancies at the interface [12], as shown in Fig. 3. The estimation of the defect density is important. This work is still in progress.

It was shown that the degraded device exhibited an analogous leakage behavior with the device which has a thin intercalated (Ba_{0.5}Sr_{0.5})TiO₃ layer with intentionally introduced oxygen vacancies between a cathode and a (Ba_{0.5}Sr_{0.5})TiO₃ layer without intentionally introduced oxygen vacancies, as shown in Fig. 2. The thin intercalated (Ba_{0.5}Sr_{0.5})TiO₃ layer with

intentionally introduced oxygen vacancies was prepared at low OMR of 3.3%. The thicker (Ba_{0.5}Sr_{0.5})TiO₃ layer without intentionally introduced oxygen vacancies was prepared at high OMR of 20%. This could be explained by assuming that oxygen vacancies accumulate at the interface between the cathode and the dielectric after fatigue. Fig. 4 shows the plot of $\ln(J_{SE})$ at 25 °C versus $V^{1/4}$ of the virgin devices ($n = 10$). The top and bottom limits of $\pm 3\sigma$ (σ is the standard deviation) are indicated in Fig. 4. As shown in Fig. 4, the reproducibility of the measurement results was confirmed.

IV. CONCLUSIONS

From our experimental and analytical results of I - V characteristics, it was shown that the degraded devices exhibited analogous leakage behaviors with the devices which have thin intercalated (Ba_{0.5}Sr_{0.5})TiO₃ layers with intentionally introduced oxygen vacancies between cathodes and thick (Ba_{0.5}Sr_{0.5})TiO₃ layers without intentionally introduced oxygen vacancies. This may be explained by assuming that oxygen vacancies accumulate at the interfaces between the cathodes and the (Ba_{0.5}Sr_{0.5})TiO₃ films after fatigue.

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