Electron-detrapping from localized states in the band gap of (Ba,Sr)TiO$_3$

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Received 28 May 2004; accepted 7 July 2004 by E.L. Ivchenko

Available online 22 July 2004

Abstract

We tried to relate the relaxation currents of Pt/62 nm-thick-(Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$/Pt capacitors to the results of ultraviolet photoemission spectroscopic measurements for the 62 nm-thick-(Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$/Pt specimens. The slowest relaxation (159–313 s at applied voltages of 1.5–3 V, and at a measuring temperature of 40 °C) and the relatively faster relaxations (4.92–5.43 and 0.25–0.46 s) were assigned as the electron-detrapping from the localized state at 0.80 eV below the quasi-Fermi level, from the localized state at 0.55 eV below the quasi-Fermi level, and from the localized state at 0.30 eV below the quasi-Fermi level, respectively. The decrease in the relaxation time caused by the increase in bias voltage is probably due to the decreasing depletion width. The decrease in depletion width is probably due to the detrapping of electrons from deep localized states in accordance with the downward bending of quasi-Fermi level in the depletion layer. The bending is produced by the decrease in relative dielectric constant in the depletion layer in accordance with the increasing of bias voltage.

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PACS: 7755+f

Keywords: A. Thin films; A. Ferroelectric

1. Introduction

Much attention has been focused on (Ba,Sr)TiO$_3$ thin films due to their potential application as dynamic random-access memories (DRAMs), and as tunable microwave devices. (Ba,Sr)TiO$_3$ thin films show slow dielectric relaxation. Slow dielectric relaxation is harmful to the frequency dependence of capacitance and dissipation factor, and to the storage charge loss during the refresh cycle of DRAMs.

There are several models of relaxation behaviors of (Ba,Sr)TiO$_3$ thin films such as the atomic rearrangement [1], the electron-detrapping [2], and the Debye-type polarizations [3]. The electron-detrapping mechanism is a reasonable one. However, real physical mechanism of the relaxation seems to be not fully understood. Therefore, we tried to define the mechanism of relaxation of (Ba$_{0.5}$Sr$_{0.5}$)-TiO$_3$ films. The relaxation behavior and the result of ultraviolet photoemission spectroscopy observed can be interpreted based on experimental and theoretical results available in the literatures for localized states in the band gap of SrTiO$_3$ or (Ba,Sr)TiO$_3$ [4–14].

2. Experiment

The Pt(250 nm)/(Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$(62 nm)/Pt(100 nm) capacitors were fabricated on TiO$_2$(2 nm)/SiO$_2$(80 nm)/Si substrates for the measurements of leakage current (I) versus time (t) characteristics.

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were fabricated on TiO$_2$(2 nm)/SiO$_2$(80 nm)/Si substrates for ultraviolet photoemission spectroscopic measurements.

The Pt bottom electrodes were deposited by dc sputtering in an ambient of argon (Ar) gases at a constant pressure of 0.7 Pa, at a constant substrate temperature of 250 °C, and at a fixed dc power of 100 W. The (Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$ films were deposited on the bottom Pt electrodes by rf magnetron sputtering in an ambient of oxygen (O$_2$) and Ar gases with O$_2$/Ar ratio of 5/5, at a constant pressure of 0.035 Pa, at a constant substrate temperature of 600 °C, and at a fixed rf power of 1 kW and a fixed dc power of 200 W. The Pt top electrodes were deposited with a diameter of 0.5 mm on the (Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$ films by electron beam evaporation at 120 °C, through a metal shadow mask. After a series of depositions, the capacitors were annealed at 600 °C in oxygen ambient for 30 min. The current versus time (I–t) characteristics were measured using a pA-meter (ADVANTEST R62469) with a constant voltage (1.5–3 V) applied to the top electrode, while the bottom electrode was grounded. The value of each measuring time was 0.1 s. The I–t measurements (for 3 capacitors) were performed at 40 °C. The ultraviolet photoemission spectroscopic measurements were performed using a model AC-2 ultraviolet photoemission spectrometer (RIKEN KEIKI Co., Ltd). The value of each measuring time was 10 s. The ultraviolet photoemission spectroscopic measurements (for 9 specimens) were performed at 25 °C in air with an incident angle of 30°. The ionization potential of (Ba$_{0.5}$-Sr$_{0.5}$)TiO$_3$ films can be obtained from the plot of d(the yield of detected electron)/d(incident photon energy) versus incident photon energy.

3. Results and discussion

As reported previously, three kinds of relaxations ($\tau_1 = 159–313$ s, $\tau_2 = 4.92–5.43$ s, and $\tau_3 = 0.25–0.46$ s) were observed from I–t characteristics at applied voltages of 1.5–3 V, and at a measuring temperature of 40 °C. These are given by:

$$I_{\text{total}} = \sum_{n=1}^{3} I_{0,n} \exp \left( -\frac{t}{\tau_n} \right)$$  \hspace{1cm} (1)

where $I_{\text{total}}$ is the total current, $I_{0,n}$ is the constant, $\tau_n$ is the relaxation time, and $t$ is the measuring time, respectively. 

Fig. 1 shows the influences of bias voltages on the relaxation times; (a) for $\tau_1$, (b) for $\tau_2$, (c) for $\tau_3$. As shown in Fig. 1(a)–(c), $\tau_1$ and $\tau_3$ decreased in accordance with the increasing of bias voltage. Furthermore, the fittings of $\tau_1$ and $\tau_3$ resemble. This can be explained by assuming that the relaxations for $\tau_1$ and for $\tau_3$ comply with the common mechanism.

The decrease in relaxation time in accordance with the increasing of bias voltage is probably due to the decreasing of depletion width ($W_{\text{dl}}$). The depletion width is proportional to $(V_{\text{bi}} + V)^{1/2}$; $V_{\text{bi}}$ denotes the built-in voltage and $V$ denotes the applied voltage, and proportional to $\varepsilon_1^{1/2}$; $\varepsilon_1$ denotes the relative dielectric constant in the depletion layer, as given by:

$$W_{\text{dl}} = \frac{2e_0\varepsilon_0(V_{\text{bi}} + V)}{qN_{\text{SC}}}^{1/2}$$  \hspace{1cm} (2)

where $\varepsilon_0$ is the dielectric constant of free space, $q$ is the electric charge of a donor-like defect (oxygen vacancy) in the depletion layer, and $N_{\text{SC}}$ is the donor-like defect density in the depletion layer. We assumed the relaxation time is given by:

$$\tau = \frac{W_{\text{dl}}}{\mu_{\text{drift}}} = \frac{W_{\text{dl}}}{\mu(V_{\text{bi}} + V)/W_{\text{dl}}} = \frac{2e_\varepsilon\varepsilon_0}{qN_{\text{SC}}\mu}$$  \hspace{1cm} (3)

Fig. 1. Influences of bias voltages on the relaxation times of Pt(250 nm)/(Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$(62 nm)/Pt(100 nm) capacitor; (a) for $\tau_1$, (b) for $\tau_2$, (c) for $\tau_3$. The measurements (for 3 capacitors) were performed at 40 °C. (d) Plot of leakage current versus ln(t), t denotes the measuring time.
where $v_{\text{drift}}$ is the drift velocity of electron, and $\mu$ is the electron mobility. Relaxation time; $\tau$ decreases in accordance with decreasing $\varepsilon_r$. Generally, the relative dielectric constant decreases exponentially in accordance with the increasing applied voltage when the applied voltage is low. Therefore, we speculate that the depletion width decreases in accordance with the increasing applied voltage when the applied voltage is low.

Relaxation time; $\tau$ may decrease in accordance with decreasing $E_a$; $E_a$ denotes the activation energy for the detrapping of electron from the potential well. Relaxation time; $\tau$ for the detrapping of electron from the potential well
can be given by:

\[ \tau = \tau_0 \exp \left( \frac{E_a}{kT} \right) \]  

(4)

where \( \tau_0 \) is the constant. \( E_a \) may decrease in accordance with the increasing of applied voltage. However, we should recall that three kinds of relaxations (159–313, 4.92–5.43, and 0.25–0.46 s) exist. And we should recall that the slow relaxation is assumed to be electron-detrapping from the deeper trap, and faster relaxation is assumed to be electron-detrapping from the relatively shallow trap.

The decrease in depletion width in accordance with the increasing applied voltage can be explained by assuming that the \( N_{SC} \) increases in accordance with the increasing of applied voltage. When the applied voltage increases, the quasi-Fermi level in the depletion layer is assumed to bend downward. This downward bending of quasi-Fermi level can eliminate electrons from the deep localized states. The positively charged ionized states can compensate for negative charges of deep-lying acceptor-like surface states near the valence band maximum. The decreasing of electrons trapped by deep localized states causes the decreasing of depletion width. Fig. 2 shows schematic energy band diagrams accounting for localized states and deep-lying acceptor states in the band gap of SrTiO\(_3\) or (Ba,Sr)TiO\(_3\), which are available in the literatures [4–14], and accounting for our relaxation model. Fig. 2(a) shows the shallow donor state which is generated by oxygen vacancies [8,12], the deep localized state which is generated by oxygen vacancies [4,5], and the deep-lying acceptor-like surface state [4,5,12] which is assumed to be generated by cation vacancies at the free surface of single crystal SrTiO\(_3\) [12]. As described in Ref. [9], proton incorporated in the Ba–O plane may generate the donor level of 0.04 eV below the conduction band minimum, and proton incorporated in the Ti–O plane may generate the donor level of 0.08 eV below the conduction band minimum. Longo et al. calculated the levels of the localized state around 0.50 eV below the conduction band minimum, the deep localized state around 1.50 eV below the conduction band minimum, and the deep-lying acceptor-like state near the valence band maximum, which are generated by incomplete atomic coordinates [14]. Fig. 2(b) shows the deep partial densities of states generated by oxygen vacancies clustering at the free surfaces of SrTiO\(_3\) films [6]. As described in Ref. [7], nontrivial local electronic structures can be generated owing to the presence of dangling bonds and incomplete atomic coordinates. Fig. 2(c) shows the deep localized states of 1.60 and 2.40 eV below the conduction band minimum which are assumed to be generated by oxygen vacancies, and shows the deep state near the valence band maximum [13]. Fig. 2(d) shows the ionized donor level of 0.15 eV below the conduction band minimum [10]. Fig. 2(e) shows our model when no bias voltage is applied. Fig. 2(f)–(h) shows the changes of band structures in accordance with the increasing of applied voltage.

Fig. 3(a) shows the result of ultraviolet photoemission spectroscopic measurement for (Ba\(_{0.5}\)Sr\(_{0.5}\))TiO\(_3\)(62 nm)/Pt(100 nm) specimen. Fig. 3(b) shows schematic energy band diagram accounting for the result of ultraviolet photoemission spectroscopic measurement. As shown in Fig. 3(a), three localized states (0.30, 0.55, and 0.80 eV below the quasi-Fermi level), which are occupied with electrons when the bias voltage is not applied, are observed. It is assumed that electrons are eliminated from these localized states when the bias voltage is applied, in accordance with the downward bending of quasi-Fermi level in the depletion layer. This may cause the decreasing of depletion width. The slowest relaxation (159–313 s) and the relatively faster relaxations (4.92–5.43 and 0.25–0.46 s) were assigned as the electron-detrapping from the localized state at 0.80 eV below the quasi-Fermi level, from the localized state at 0.55 eV below the quasi-Fermi level, and from the localized state at 0.30 eV below the quasi-Fermi level, respectively. It is speculated that the three localized states are generated by the lattice strain at the surface of
4. Conclusions

The relaxation behaviors of Pt/(Ba0.5Sr0.5)TiO3/Pt capacitors can be related to the results of ultraviolet photoemission spectroscopic measurements for the (Ba0.5Sr0.5)TiO3/Pt specimens. The slowest relaxation (159–313 s at applied voltages of 1.5–3 V, and at a measuring temperature of 40 °C) and the relatively faster relaxations (4.92–5.43 and 0.25–0.46 s) were assigned as the electron-detrapping from the localized state at 0.80 eV below the quasi-Fermi level, from the localized state at 0.55 eV below the quasi-Fermi level, and from the localized state at 0.30 eV below the quasi-Fermi level, respectively. The decrease in relaxation time induced by the increasing bias voltage is probably due to the decrease in depletion width. The decrease in depletion width is probably due to the clustering of oxygen vacancy at the surface of (Ba0.5Sr0.5)TiO3, and are generated by oxygen vacancy clustering at the surface of (Ba0.5Sr0.5)TiO3.

Fig. 3. (a) The result of ultraviolet photoemission spectroscopic measurement for (Ba0.5Sr0.5)TiO3(62 nm)/Pt(100 nm) specimen. The measurements (for 9 specimens) were performed at 25 °C in air. The ionization potential of (Ba0.5Sr0.5)TiO3 films can be obtained from the plot of d(yield of detected electron)/d(incident photon energy) versus incident photon energy. (b) Schematic energy band diagram accounting for the result of ultraviolet photoemission spectroscopic measurement.
detrapping of electrons from deep localized states in accordance with the downward bending of quasi-Fermi level in the depletion layer, and due to the decrease in relative dielectric constant in the depletion layer in accordance with the increasing bias voltage.

References