Capacitance and admittance spectroscopy analysis of hydrogen-degraded Pt/(Ba, Sr)TiO_3/Pt thin-film capacitors

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(Received 8 May 2000; accepted for publication 25 July 2000)

One of the problems occurring in conjunction with the integration of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin film capacitors into the Si technology is the large increase of leakage current after a forming gas heat treatment. In order to reveal the underlying mechanism, we studied the electric properties of Pt/BST/Pt (metal–insulator–metal) (MIM) structures after annealing in atmospheres containing hydrogen (H_2) or carbon monoxide by means of admittance spectroscopy. Frequency-dependent capacitance measurements on these MIM structures revealed a thermally activated relaxation step at low frequencies with an activation energy of 0.62 eV. Admittance spectroscopy, in which the conductance is monitored as a function of temperature and frequency, verifies the Schottky barrier heights at the Pt/BST interface revealed by dc measurements. We found that the Schottky barrier height decreased by 0.4 eV after annealing in a reducing atmosphere, independent of the presence of protons. © *2000 American Institute of Physics.* [S0003-6951(00)00139-X]

Because of rapid evolution in the integration technology of high-dielectric-constant ferroelectric materials like $Ba_{0.7}Sr_{0.3}TiO_3$ (BST), the integration of ferroelectric capacitors in complementary metal–oxide–semiconductor (CMOS)-based devices is one of the most important challenges.[1,2] For practical device applications of these new materials, their electrical properties must be understood properly with respect to dependence on the CMOS-integration processes. One of the most serious problems that Pt/BST/Pt ferroelectric capacitors suffer from during integration is the large increase of the leakage current by more than four orders of magnitude after annealing in a strongly reducing atmosphere,[3,4] e.g., a typical forming gas anneal (N_2 95% and H_2 5%). To avoid dramatical resistance degradation it is important to determine its origin.

BST films, typically 130 nm thick, were deposited by chemical solution deposition (CSD)[3,5] on a platinized Si wafer. The Pt top electrodes (100 nm) were deposited by rf magnetron sputtering and patterned by a lift off process. The surface area of the top electrodes is 0.19 mm^2. The resulting capacitors were postannealed under an oxygen atmosphere at $T = 550–600$ °C for 30 min, and are referred to as the reference capacitors. Additionally, some capacitors were annealed at $T = 450$ °C under a forming gas atmosphere (FGA) or a mixture of CO 5% and argon 95% (COA). These atmospheres have comparable oxygen partial pressure p_{O_2}, which are lower than 10^{-15} bar. The electrical data were acquired using a Keithley 617 electrometer as the voltage source and picoamperemeter. A voltage-step technique is used to precisely reveal the leakage currents and to eliminate dielectric charging currents of the capacitor. For ac measurements a frequency response analyzer SI1260 from Schlumberger Ltd. was used in combination with a Solatron 1296 dielectric interface.

Figure 1(a) shows comparison of the leakage current for a Pt/BST/Pt capacitor before and after a reducing atmosphere heat treatment at 450 °C. The leakage current increases by more than four orders of magnitude, whereas the COA-treated samples still show a higher leakage current than the forming gas annealed samples. Some samples were recovery annealed in air at very low temperatures for 30 min on a hot plate. Figure 1(b) shows the leakage current of a capacitor at an applied voltage of 2 V as a function of the recovery temperature. It is clearly observed that around 150 °C the leakage current density at an applied voltage of 2 V decreases rapidly. Both the FGA- and COA-treated samples show this recovery annealing behavior.

The capacitance of the test structures was measured as a function of frequency at different temperatures at zero voltage dc bias. In the case of the FGA- and COA-treated samples the capacitance shows a Debye-like relaxation be-

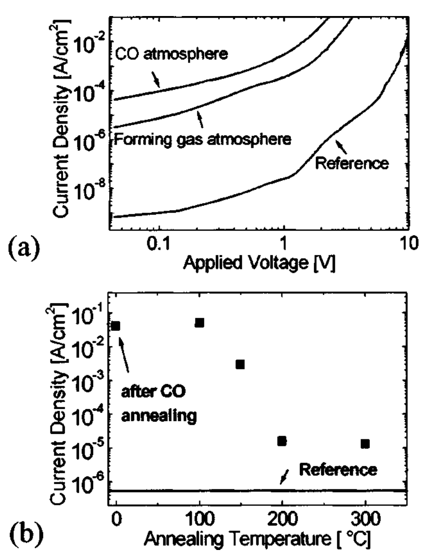

FIG. 1. (a) Variation of the leakage current density of the Pt/BST/Pt capacitors annealed under the forming gas and CO containing Ar in comparison to the reference capacitor and (b) leakage current at an applied voltage of 2 V as a function of the recovery annealing temperature.

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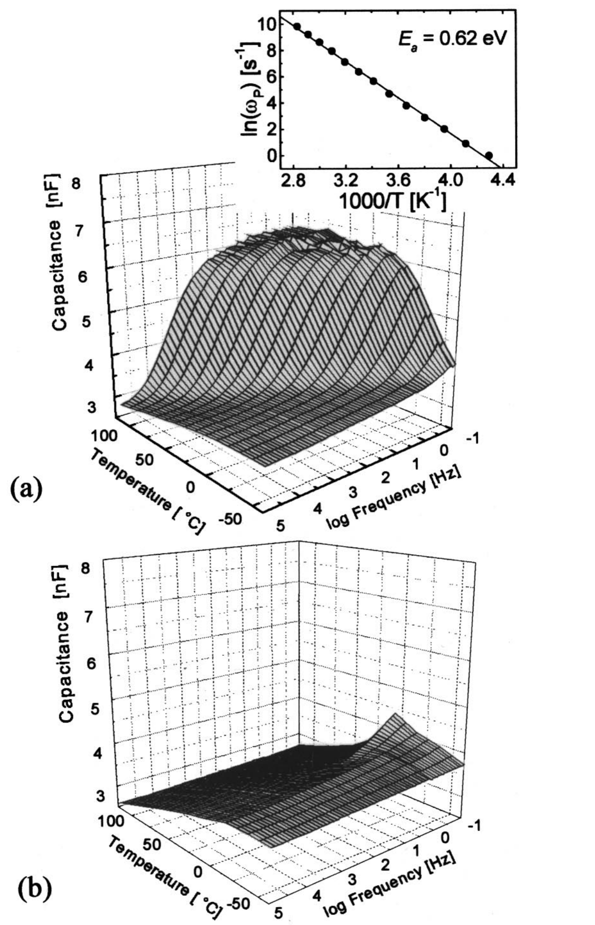

FIG. 2. Temperature and frequency dependence of the capacitance for (a) the FGA-annealed capacitors and (b) the capacitors recovered in air at $T=200\,°\mathrm{C}$.

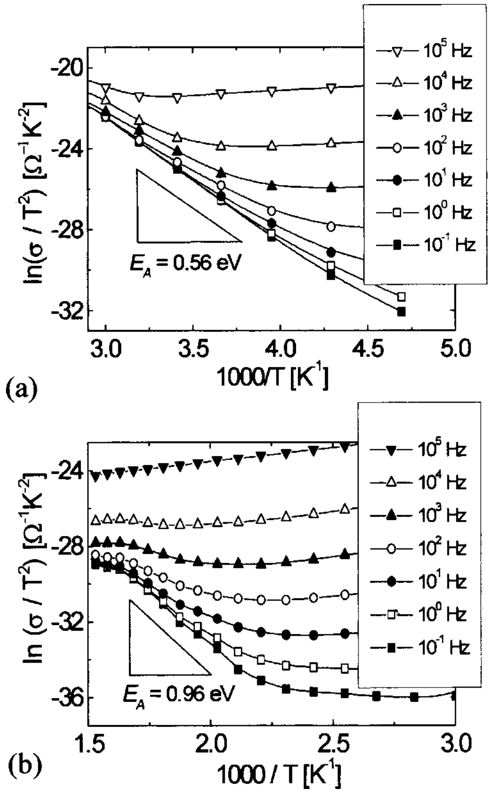

FIG. 3. Relation between $\ln(\sigma/T^2)$ and $1000/T$ as a function of frequency for (a) the FGA-annealed capacitors and (b) the capacitors recovered in air at $T=200\,°\mathrm{C}$.

havior with a relaxation step height of $\Delta C = C_{lf} - C_{hf} \approx 3\,\mathrm{nF}$ [Fig. 2(a)]. The measured capacitance can be expressed by

$$C_p(\omega,T) = C_{hf} + \frac{C_{lf}-C_{hf}}{1+(\omega/\omega_p)^2}, \quad (1)$$

where C_{lf} is the capacitance measured at low frequency ($\omega \ll \omega_p$), and C_{hf} is the capacitance measured at high frequency ($\omega \gg \omega_p$). The temperature dependence of the relaxation frequency ω_p is given by

$$\omega_p = \omega_0 \exp(-E_a/k_b T), \quad (2)$$

where ω_0 is the characteristic relaxation frequency at infinite temperature, E_a is the activation energy for relaxation, k_b Boltzmann's constant, and T the absolute temperature. The measured data [see insert of Fig. 2(a)] reveal an activation energy of 0.62 eV. After low temperature annealing at $T=200\,°\mathrm{C}$ in air, the relaxation step disappears [Fig. 2(b)] and the capacitance shows only a slight dependence of the frequency.

The current conduction through Pt/BST/Pt thin films capacitors is usually controlled by the interfacial potential barrier, of which the magnitude is affected by the work function of the contacting metal and interface trap states.[6–9] The leakage current in such a MIM structure is assumed to be determinded by the reversed biased Schottky contacts with the Schottky barrier height Φ_b. Although additional conduction mechanisms like tunneling at the Pt–BST interface are discussed[10] the leakage current data in this article were analyzed with respect to Schottky conduction.

In order to determine the zero-voltage Schottky barrier height Φ_b^0 the admittance was measured as a function of frequency at different temperatures with an ac signal of 30 mV. The temperature dependence of $\ln(\sigma/T^2)$ of the MIM structure after FGA and after the subsequent recovery annealing at $T=200\,°\mathrm{C}$ is shown in Figs. 3(a) and 3(b), respectively. It is obvious that in the low-temperature regime, the ac conductivities depend significantly on the frequency. If the temperature is increased a linear relation between $\ln(\sigma/T^2)$ and $1/T$ becomes apparent. The activation energies were determined from the slope in this region for the FGA-treated samples as $E_a^{\mathrm{FGA}} = 0.56\,\mathrm{eV}$ and for the recovered samples as $E_a^{\mathrm{REC}} = 0.96\,\mathrm{eV}$, respectively. These activation energies should now be compared to the zero-voltage Schottky barrier height determined by dc measurements.

The experimental procedure for determining the Schottky barrier heights from dc measurements is described elsewhere.[7,8] For the same set of samples the zero-voltage Schottky barrier height was measured for the top and bottom contacts and for the FGA and recovered samples (Fig. 4). The activation energies which are shown in Table I are in very good agreement with the zero-voltage Schottky barrier heights determined by dc measurements, both techniques revealed a lowering of the Schottky barrier height after a reducing heat treatment of about $\Delta\Phi_b^0 \sim 0.4\,\mathrm{eV}$.

The physical origin of the large increase of the leakage current after the forming gas anneal has been discussed in the literature from different point of views. It is known that hy-

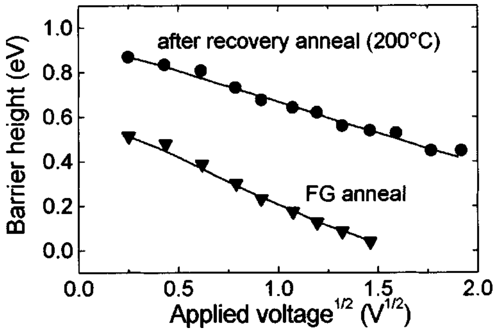

FIG. 4. Variations of the Schottky barrier heights as a function of $\sqrt{V}$ for Pt/BST/Pt capacitor after FG anneal and after a subsequent low temperature recovery anneal in air at $T=200\,°C$ (top electrode positively biased).

drogen dissolves within the BST lattice during FGA.[11] The dissociation process of molecular hydrogen should be supported by the catalytic nature of the Pt surface.[12] The H^+ ions then diffuse through the Pt layer and accumulate in the BST thin film. The increase of leakage current was then attributed to the lowering of the Schottky barrier by an interface hydrogen layer.[3,13] Due to the comparable degradation of BST thin film capacitors in forming gas and a CO-containing Ar atmosphere we can clearly exclude the presence of dissolved hydrogen in the BST lattice as a reason for the increase in leakage current.

After oxidizing treatment (i.e., initially or after the recovery anneal) the film shows a high resistivity throughout its entire thickness. We suggest that due to annealing in a reducing atmosphere oxygen vacancies are produced ($O_0 = V_0^{\cdot\cdot} + 2e^- + 1/2O_2$) and a layer of lower resistivity (ϱ_L) is generated within the film. Based on the impedance spectra

TABLE I. Zero-voltage Schottky barrier heights Φ_b^0 for FGA-annealed and recovered Pt/BST contacts in comparison to the activation energies determined by ac measurements.

	FGA	recovered at $T=200\,°C$
dc(+)[a]	0.6 eV	1.05 eV
dc(−)[a]	0.55 eV	0.95 eV
ac	0.56 eV	0.96 eV

[a]Bias of the top electrode.

and the assumption that the real permittivity of the BST does not change drastically during FG anneal, we can state from the ratio of C_{lf} and C_{hf} that the layer of low resisitivity, ϱ_L, consumes approximately 50% of the film thickness. According to the Maxwell Wagner[14] relaxation model of serial RC combinations of two layer within the film the ratio of the resistivities of the high resistive (ϱ_H) and the low resistive (ϱ_L) layer can be estimated to be $\varrho_L/\varrho_H \sim 0.1$. The physical origin and the location of the highly resistive layer which remains after FG anneal are still under investigation. Possibly it is located at the interfaces and is generated by carrier depletion. Additionally, we suppose that interface trap states are generated. These interface trap states, which create an interface dipole,[15] reduce the zero voltage Schottky barrier height of about 0.4 eV. In conclusion, protons are not the origin of the increase of leakage current in Pt/BST/Pt MIM structures after a forming gas anneal. It was found that the zero voltage Schottky barrier height was decreased by approximately 0.4 eV after a reducing heat treatment, which was measured by ac and dc experiments. The strong Debye-like relaxation steps in the capacitance at low frequencies was discussed by means of Maxwell Wagner relaxation.

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