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Mechanism of low temperature hydrogen-annealing-induced degradation in $Pb(Zr_{0.4}Ti_{0.6})O_3$ capacitors

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Changes in the polarization–field hysteresis loop were systematically investigated for $Pb(Zr_{0.4}Ti_{0.6})O_3$ capacitors after forming gas annealing at 200 °C. Voltage shift in hysteresis was strongly dependent on the polarization states and ascribed to an asymmetric distribution of defect charges and pinned defect dipoles. Field recovery of the imprinted capacitors and increase in coercive field after the recovery were discussed in conjunction with reversible defect dipoles. From the relaxation of the voltage shift with an activation energy of 0.21 eV, it is inferred that charge trapping may be the main cause of the voltage shift and the subsequent degradation of the capacitors by pinning the polarization and defect dipoles.
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Hydrogen-induced degradation is an important problem that should be understood for the realization of reliable ferroelectric nonvolatile memory devices. During the integration processes of the devices, the ferroelectric capacitors are exposed to a reducing ambient, such as hydrogen-containing forming gas, and degrade to result in the loss of ferroelectricity.[1–6] Especially, $Pb(Zr,Ti)O_3$ (PZT) capacitors with Pt electrodes are easily degraded by forming gas annealing (FGA) even at the temperature as low as 100 °C. Although, in PZT, formation of oxygen vacancies has been implicated as playing a role in the major failure mechanisms, oxygen loss may not be significant enough to account for the degradation at the low temperature FGA.

As for the low temperature FGA-induced degradation, the incorporation of hydrogen ions has been suggested as the prime mechanism such that the formation of OH^- polar bonds, which can act as defect dipoles, prevent ferroelectric polarization from switching in PZT.[7,8] Recently, the energy barrier for the reversal of OH^- in PZT has been estimated to be about 0.2 eV.[9] However, such a low value of energy barrier does not seem to guarantee the active role of OH^- in preventing polarization switching.

In this work, we focused attention on the low temperature FGA-induced degradation of PZT capacitors by investigating imprint and relaxation of the voltage shift, and effects of trapped defect charges and defect dipoles (D_d) (possibly OH^-) were emphasized. Trapped charges, which pin ferroelectric polarization and D_d, were suggested to be the main cause of the low temperature FGA-induced degradation in PZT.

PZT capacitors with Pt top electrodes were prepared using $Pb(Zr_{0.4}Ti_{0.6})O_3$ thin films of 200 nm thickness deposited by a chemical solution deposition on $Pt(111)/Ti/SiO_2/Si$ substrates. The test capacitors with a size of $100\times 100\ \mu m^2$ were outlined by a photolithographic lift-off process, followed by etching the uncovered PZT layer. The PZT capacitors were exposed to forming gas ($Ar+4\%H_2$) at 200 °C. Polarization was measured by RT66A and capacitance measurements were carried out using HP4284 LCR meter at 100 kHz with an ac signal of 25 mV.

Figure 1(a) shows the polarization–field ($P-E$) hysteresis loops for the PZT capacitors after FGA at 200 °C with different annealing time. Similar results were observed by other workers.[10,11] When the capacitors were poled before FGA by applying negative voltage to the top electrode, the hysteresis loops, displayed as the solid lines, showed an imprint phenomenon. The corresponding voltage shifts show a systematic increase in terms of FGA time. For the unpoled capacitors, the hysteresis loops, displayed as the dotted lines, have constricted shape. The constricted hysteresis loop became nearly dielectric after FGA for 330 min. However, the constricted hysteresis loops observed in the unpoled PZT capacitors were explained by the switching of oppositely imprinted ferroelectric domains.[10,11] Such domain switching can be probed by measuring a small signal capacitance–voltage ($C-V$) curve since the dielectric constant $\epsilon = dP/dE$ is sensitive to the polarization switching. Before FGA, the $C-V$ curve shows a sharp peak near coercive voltage due to ferroelectric polarization switching, as shown in Fig. 1(b). After FGA for 330 min, backswitching of polarization in strongly imprinted domains was manifested as a broad maximum before polarization switching occurred in both scan directions. These $C-V$ results confirm that each oppositely pinned ferroelectric domain responds separately to electric field without significant loss of feroelectricity after FGA. Therefore, Figs. 1(a) and 1(b) demonstrate clearly that the degradation induced by the low temperature FGA is

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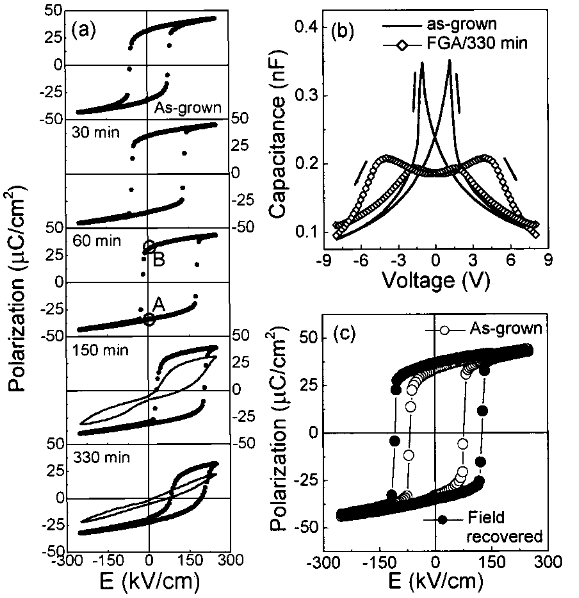

FIG. 1. (a) $P-E$ hysteresis loops for Pt/PZT/Pt capacitors after FGA at 200 °C with different annealing time (solid circles: poled with negative voltage before FGA, solid lines: unpoled capacitors). (b) $C-V$ curves for the unpoled capacitors before (solid line) and after FGA at 200 °C for 330 min (◇). (c) Comparison of $P-E$ hysteresis for a capacitor before FGA (○) and for a FG annealed one after field recovery (●). The increase of E_c is seen.

closely related with the imprint phenomenon.

The imprint might be originated from an asymmetric distribution of defect-induced space charges near the film/electrode interfaces and/or irreversible D_d. It is known that the irreversible D_d can result in a shifted or constricted hysteresis loop.[12] Further insights on the effects of the space charges and D_d can be obtained by the fact that the shifted (or constricted) hysteresis loops could be recovered by dc (or square-wave) electric field, as shown in Fig. 1(c). The field recovery is related to the emission of trapped charges and redistribution of the defect charges. Note that the remnant polarization P_r and the coercive field E_c after the recovery become larger than those before the recovery. A close look at Fig. 1(a) shows that such increases occur at the early stage of the FGA. These increases could be attributed to the reversible D_d formed during the FGA. If the D_d are reversible by field, they generally increase P_r and E_c without a voltage shift of $P-E$ hysteresis.[12] Thus, the field recovery of shifted hysteresis loops [Fig. 1(c)] implies that D_d should be reversible.

The reversibility and the generation of D_d at the low temperature FGA suggest that OH^- may be the most probable candidate for the D_d. During the FGA process, several kinds of D_d can be induced inside ferroelectric thin films; Pt impurity-oxygen vacancy,[13] Pb vacancy-oxygen vacancy complexes,[14] OH^-, etc. However, most D_d, except for those involving H^+ ions, may be formed at high temperature FGA and irreversible because of the low mobility of oxygen vacancies at room temperature. In fact, Raman scattering[7,8] has shown the existence of the OH^- in the FG-treated PZT capacitors. More significantly, the recent first-principles total-energy calculations have shown that the energy barrier for the reversal of OH^- dipole is about 0.2 eV.[9] Considering the phonon-assisted hopping process, the hopping transition of the H^+ ions between the opposite sites is estimated to occur around 10 ns, so OH^- itself could be easily reversible. Thus, OH^- cannot prevent polarization switching. Together with the results shown in Fig. 1(a), it can be inferred that the low temperature FGA does not suppress ferroelectric polarization significantly but induces charged defects whose pinning effect might be the main cause of the voltage shift and the subsequent degradation. If the OH^- were pinned by charged defects, they can contribute additively to the voltage shift and the degradation.

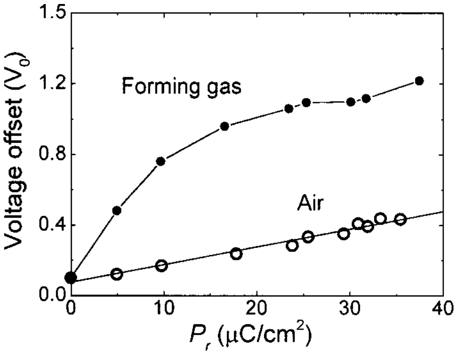

FIG. 2. P_r dependencies of voltage shift for air annealed (○) and FG annealed (●) capacitors.

Actually, FGA can produce high density of defect charges and D_d; H^+ ions, electrons, OH^- dipoles, and other complexes. These defects may interact with polarization resulting in the large voltage shifts. To test this idea, several PZT capacitors of different P_r states were prepared by taking $P-E$ loops with different maximum bias, and then annealed at 200 °C for 60 min in air or in FG. The magnitude of the voltage shift (offset), $V_0 = (V_c^+ + V_c^-)/2$ (where $V_c^\pm$ is the voltage at zero polarization in the hysteresis loop), was measured as a function of P_r. As shown in Fig. 2, FGA-induced V_0 was much larger than the air-annealing induced one at the same P_r, indicating that much more charged defects, including OH^- dipoles, are produced. In addition, the FGA-induced V_0 showed a nonlinear dependence on P_r, in contrast to that of the air-annealed sample where V_0 is proportional to P_r. It has been reported that polarization can change occupancy of traps by affecting the potential well for the trapped electrons.[15,16]

It was found that the voltage shifts of the moderately imprinted capacitors could be relaxed to the opposite direction, if the polarization state became reversed. The relaxation process triggered by the polarization reversal can provide information on the redistribution/detrapping of defect charges. To investigate the relaxation process about 40 different PZT capacitors with the same size and thickness were prepared to have the same initial voltage offset $[V_0(t=0) = 1.2\ \mathrm{V}]$ after FGA. The variation of $V_0(t=0)$ for the capacitors was found to be less than 4%. Then, their polarization states were reversed from A to B, as indicated in Fig. 1(a), by taking a $P-E$ loop in the reverse direction. The capacitors were stored at various temperatures (25, 50, 75, and 100 °C). After a given waiting time, $V_0(t)$ for each different capacitor was measured by taking $P-E$ loops.

Figure 3 shows the relaxation of the voltage shift, $V_0(t)$, as a function of waiting time at various temperatures. A rapid relaxation of voltage shift was followed by a slow one at each temperature. The overall relaxation could be described

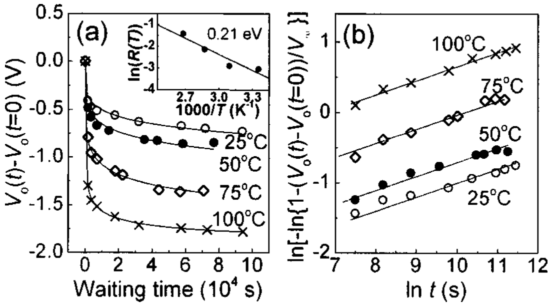

FIG. 3. (a) Polarization-triggered relaxation of voltage offset as a function of waiting time at different temperatures; 25 (○), 50 (●), 75 (◇), and 100 °C (×). Capacitors were FG annealed at 200 °C for 90 min after poling. The inset shows the fit of $\ln[R(T)]$. (b) The linear fit shows the relation between $\ln\{\ln[1-(V_0(t)-V_0(t=0))/V_\infty]\}$ and $\ln t$ at each temperature. The slope is the exponent $n=0.2\pm0.03$ of the stretched exponential equation.

by a stretched exponential equation, $[V_0(t)-V_0(t=0)]/V_\infty = 1-\exp[-R(T)t^n]$,[17] with an averaged exponent value of $n=0.2\pm0.03$. Activation energy E_a for the relaxation was obtained to be about 0.21 eV from Arrhenius-type equation

$$R(T)=R_0 \exp\left(-\frac{E_a}{kT}\right), \tag{1}$$

where R_0 is a pre-exponential factor and k is the Boltzmann constant. (It should be noted that the slow relaxation part after 3×10^3 s could be fitted with a simple exponential function. The corresponding activation energy was also determined to be about 0.2 eV.) The relaxation of voltage shift is believed to be due to the emission of trapped charges and their redistribution by the polarization-induced internal field. Then $R(T)$ can be thought of as the emission rate of trapped charges and the activation energy is considered as the corresponding trap level. The stretched exponential behavior may be due to many trapping/detrapping processes occurring during the relaxation.

In summary, FGA-induced imprint and polarization-triggered relaxation of the voltage offset were investigated for degraded PZT during the low temperature FGA. Effects of defect charges and reversible OH^- dipoles were discussed in conjunction with the voltage shift of $P-E$ loops and their field recovery. Emission of trapped charges and their redistribution by the internal field were suggested to be responsible for the relaxation of the voltage offset with an activation energy of about 0.21 eV. It is inferred that polarization pinning effect due to trapped charges may be the main cause of the voltage shift and the degradation induced by the low temperature FGA.

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