Degradation of Ferroelectric Properties of Pt/PZT/Pt Capacitors in Hydrogen-containing Environment

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The ferroelectric properties of the Pt/PZT($Pb(Zr,Ti)O_3$)/Pt capacitors are severely degraded when they are annealed in hydrogen-containing environment. Hydrogen atoms created by the catalytic reaction of Pt top electrode during annealing in hydrogen ambient penetrate into PZT films and generate oxygen vacancies by the reduction of the PZT films, which is likely to cause the degradation. The degree of hydrogen-induced degradation and the direction of voltage shift in P-E curves of the pre-poled PZT capacitors after annealing in hydrogen ambient is dependent on the polarity of the pre-poling voltage. This implies that oxygen vacancies causing hydrogen-induced degradation are generated by hydrogen ions having a polarity. The degraded ferroelectricity of the PZT capacitors can be effectively recovered by the shift of oxygen vacancies toward the Pt top electrode interface during post-annealing in oxygen environment with applying negative unipolar stressing.

Keywords : PZT, Degradation, Hydrogen, Pt

1. INTRODUCTION

Ferroelectric materials have two stable polarization states even when the electric field is removed. A ferroelectric random access memory (FRAM) is a memory that makes use of the two states as two storage signals, "0" and "1". FRAM has attracted considerable attention because it has many advantages such as nonvolatile memory, fast read and write speed, high endurance, and high potential for integration due to its dynamic random access memory (DRAM)-like cell structure[1]. Lead zirconate titanate (PZT) is the most promising material for use as a capacitor of FRAM devices because it has a high phase transition temperature (T_c), a high remanent polarization (P_r), and a relatively low fabrication temperature.

A study on FRAM devices has been carried out in the field of processing development for an excellent ferroelectric capacitor such as the improvement of ferroelectric material, electrode material, and electrode configuration. Recently, research field has moved toward the realization of high-density ferroelectric memory devices by improving the reliability comparable to existing ultra large scale integration (ULSI) devices and the compatibility with conventional complementary metal oxide semiconductor (CMOS) processing[2,3]. In the integration of ferroelectric capacitor, the reliability after CMOS back-end processes must be guaranteed. However, it has been reported that the polarization characteristics of Pt/PZT/Pt capacitors can be easily degraded when the ferroelectric capacitor is exposed to hydrogen-containing environments such as the deposition process of interlayer dielectric (ILD) or passivation layers[4-9]. This hydrogen-induced degradation depends strongly on the top electrode material and, in particular, the degradation is quite severe when Pt is used as a top electrode[4,5].

In order to solve hydrogen-induced degradation problem, studies have been conducted on the development of new capacitor structures that are tolerant of hydrogen-induced degradation and new processing ambient that minimizes hydrogen effects. However, fundamental studies on the hydrogen-induced degradation mechanism for the Pt/PZT/Pt thin film capacitor have been performed little so far. Thus, in this research, the effects of Pt top electrode on the hydrogen-induced degradation and the recovery of the degraded polarization properties after post-annealing were investigated by examining the electrical properties of the PZT capacitors and analyzing the hydrogen concentration in the PZT films. The effects of the polarization states of the PZT films on the hydrogen-

induced degradation and the effects of electrical stressing on the recovery of polarization properties were also studied.

2. EXPERIMENTS

Two kinds of PZT film were used for this study: random oriented PZT films and (001) preferred oriented PZT films. The random oriented PZT films were fabricated to investigate the hydrogen-induced degradation behavior with the existence of Pt top electrodes and the recovery behavior by post-annealing. The 190 nm thick PZT films were deposited onto $Pt/Ti/SiO_2/Si$ substrates by reactive sputtering under the following conditions: a deposition temperature of 475 °C, a flow rate of O_2:Ar=2:10 sccm, and a process pressure of 4 mTorr. The (001) preferred oriented PZT films having superior polarization characteristics were fabricated to investigate the effects of the polarization states of the PZT films on the hydrogen-induced degradation behavior. The 210 nm thick PZT(001) films were deposited on Pt(001)/MgO(001) substrates by sol-gel method. The (001) preferred orientation of the PZT films was confirmed by x-ray diffraction (XRD) pattern obtained with the Bragg-Brentano method as shown in Fig. 1. The composition of PZT films analyzed by wavelength dispersive spectroscopy (WDS) was Pb/(Zr+Ti)=1 and Zr/Ti=50/50. For electrical characterization, Pt top electrodes with a thickness of 200 nm were sputter-deposited at room temperature with a shadow mask. Rapid thermal annealing (RTA) was carried out at 650 °C for 1 min in oxygen environment to release the damage formed during the top electrode fabrication process.

The Pt/PZT/Pt capacitors were annealed in hydrogen environment (hereafter this process is called H_2 annealing) under various conditions and the degradation behaviors of the capacitors were investigated. The degradation by H_2 annealing became severer with increasing annealing temperature as well as with increasing hydrogen contents in the annealing furnace. In this paper, H_2 annealing was performed in H_2(3 %)/N_2 mixture gas system at an annealing temperature of 200 °C. Secondary ion mass spectrometry (SIMS) with Cs^+ primary ion (ion energy, 14.5 keV; ion beam current, 5 nA) was used to analyze the hydrogen concentration in the PZT films.

To study the degradation behavior by H_2 annealing, the polarization versus electric field (P-E) hysteresis characteristics and the relative permittivity versus voltage (ε_r-V) characteristics of the PZT capacitors were measured before and after H_2 annealing. P-E hysteresis characteristics were measured with a standard Sawyer-Tower circuit. Triangular input signal with a frequency

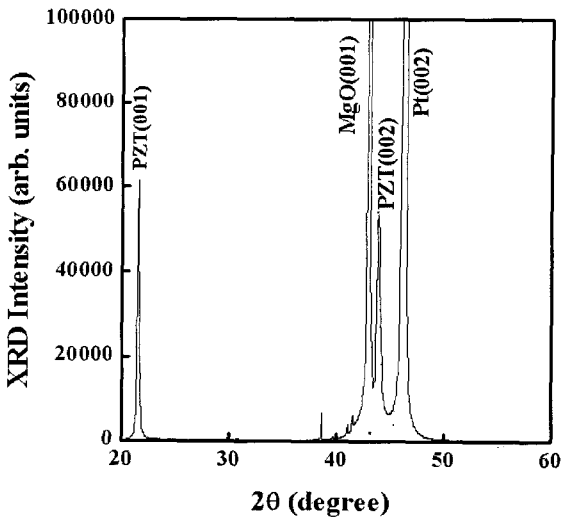

Fig. 1. XRD patterns of PZT(001) films deposited on Pt(001)/MgO(001) substrates.

of 1 kHz was applied to the top electrode by a function generator (HP 8111A) and then the voltage drop across a linear integrating capacitor of 1 nF was measured by digital oscilloscope (TDS 3032). The ε_r-V characteristics were measured by impedance/gain phase analyzer (HP4194A) under the following conditions: sweep voltages ranging from −5 V to +5 V, an ac oscillation level of 30 mV, and a delay time of 100 ms.

3. RESULTS AND DISCUSSION

To identify the role of Pt top electrode during H_2 annealing, the hydrogen-induced degradation behavior with the existence of Pt top electrode was investigated. The random oriented PZT films were annealed in H_2(3 %)/N_2 gas system at 200 °C for 20 min. Figure 2(a) shows the ε_r-V characteristics of three kinds of PZT films: S1, the virgin sample before H_2 annealing; S2, the sample experienced in H_2 annealing with Pt top electrode; S3, the sample experienced in H_2 annealing prior to the deposition of Pt top electrode. The ferroelectric property of S2 was severely degraded, whereas that of S3 was not. The hydrogen concentrations in the PZT films before and after H_2 annealing were analyzed by SIMS (Fig. 2(b)). The hydrogen concentration in the degraded PZT film (S2) was ten times higher than that of the virgin PZT film (S1). For the PZT film annealed in hydrogen environment without Pt top electrode (S3), however, the hydrogen concentration did not increase after H_2 annealing. This implies that the degradation is related with the penetration of hydrogen into the PZT film and the Pt electrode plays an important role in the penetration of hydrogen. This can be easily

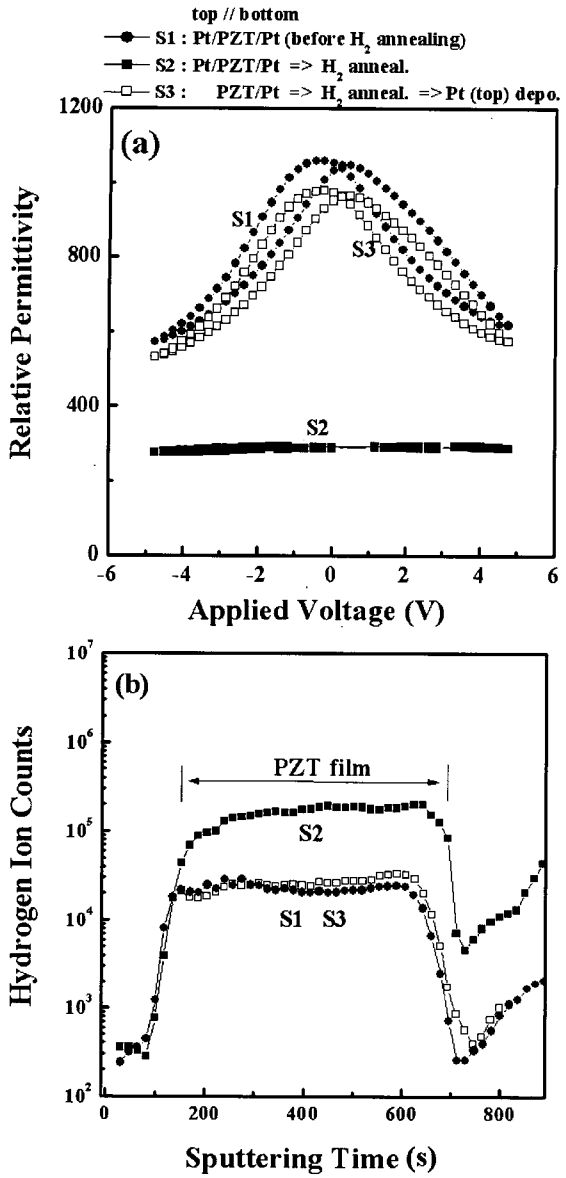

Fig. 2. (a) C-V characteristics and (b) SIMS hydrogen depth profiles of Pt/PZT/Pt capacitors.

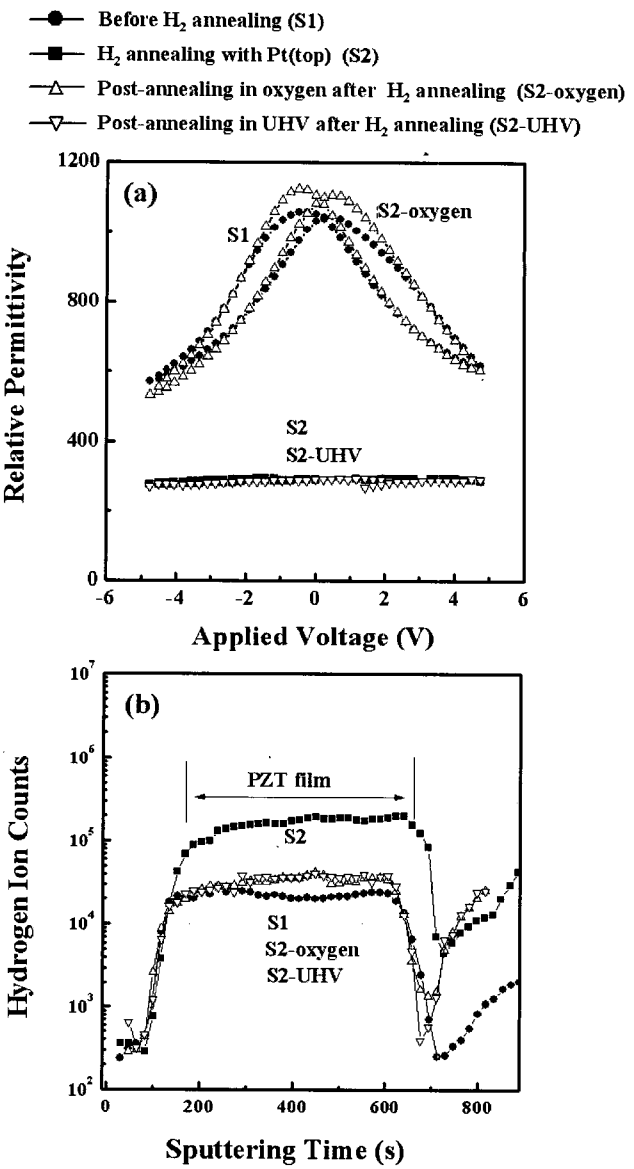

Fig. 3. Effects of post-annealing environment on (a) $\varepsilon_r - V$ characteristics and (b) SIMS hydrogen depth profiles of Pt/PZT/Pt capacitors.

understood from the fact that Pt whose d-orbital is empty is a strong catalyst for dissociating hydrogen molecules into atomic hydrogen[10]. Since the diffusivity of molecular hydrogen is quite lower than that of atomic hydrogen, the PZT film is not degraded by H_2 annealing without Pt top electrode.

Post-annealing was carried out at 400 °C for 1 min to recover the ferroelectricity of the PZT film degraded by H_2 annealing (S2). To investigate the roles of hydrogen and oxygen vacancy in hydrogen-induced degradation, post-annealing was carried out in oxygen (150 Torr) and in ultra high vacuum (UHV, 10^{-9} Torr). Figure 3(a) shows the effect of post-annealing performed in oxygen and UHV on the ε_r-V characteristics of the PZT films. The degraded ferroelectricity was recovered by the post-annealing in oxygen (S2-oxygen), but not by the post-annealing in UHV (S2-UHV). Figure 3(b) shows the SIMS hydrogen depth profiles of the PZT films after post-annealing. Regardless of the environment of post-annealing, the hydrogen concentration was reduced to almost the same level as that of the virgin PZT film (S1). However, the degraded ferroelectricity was not recovered by the post-annealing in UHV where no oxygen exists. This result indicates that the recovery of the degraded ferroelectricity is achieved not by the elimination of hydrogen from the PZT films but by the supply of

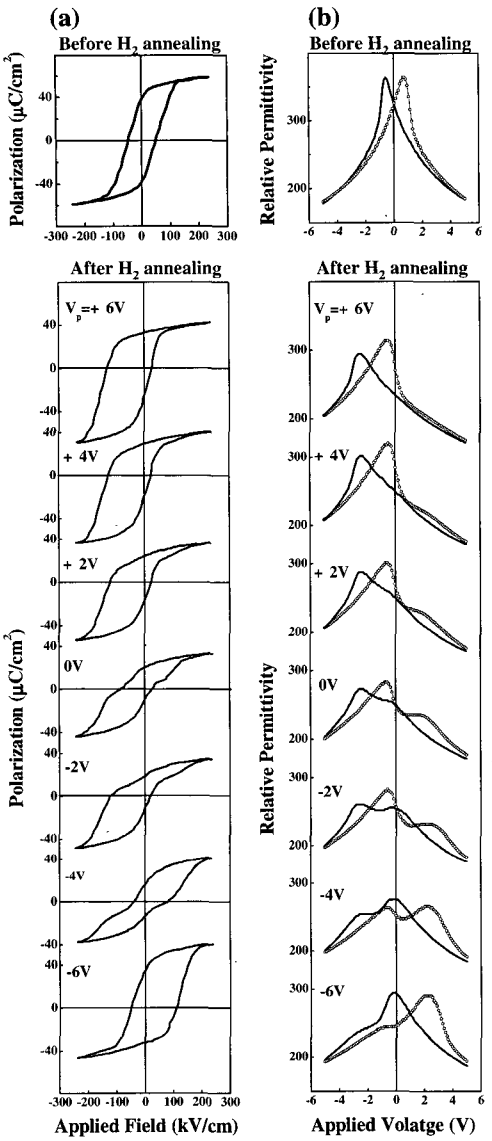

Fig. 4. Variation of (a) P-E hysteresis curves and (b) $\varepsilon_r - V$ characteristics after hydrogen annealing at 200 °C for 30 min with the pre-poling voltages (V_p) for Pt/PZT(001)/Pt capacitors.

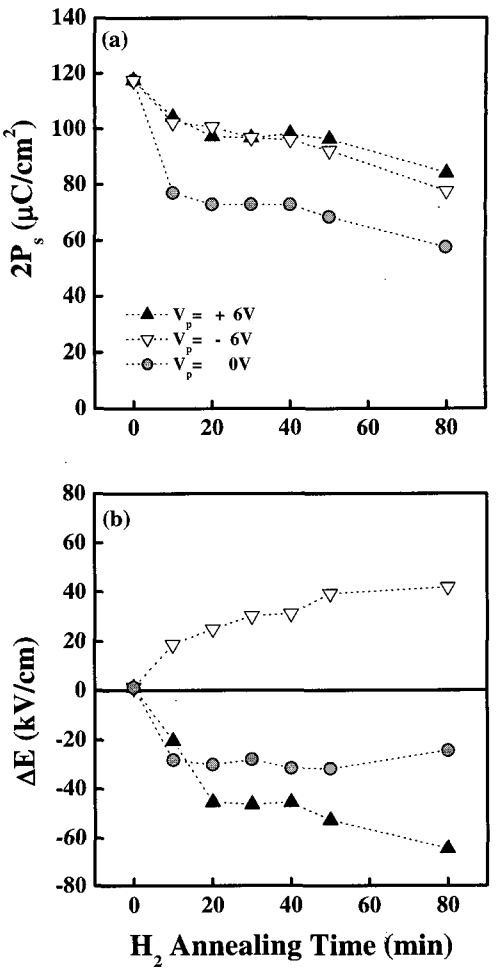

Fig. 5. Variations of (a) saturation polarization ($2P_s$) and (b) voltage shift ($\triangle E$) for the pre-poled and virgin Pt/PZT(001)/Pt capacitors with annealing time in hydrogen environment at 200 °C.

oxygen to the film. Some researchers[4-6] have believed that the degradation of ferroelectricity by H_2 annealing is due to the oxygen vacancies created by hydrogen atoms. On the other hand, T. Hase *et al.*[7] suggested that the hydrogen-induced degradation is related with the O-H bond formed within the PZT film. The result of this research implies that the hydrogen-induced degradation is not directly related with the hydrogen-related bond formed within the PZT film but is related with the oxygen vacancies created during the reduction of PZT by hydrogen atoms.

The effects of polarization states of PZT capacitors on the hydrogen-induced degradation behavior were studied. We used (001) preferred oriented PZT films for this study because they were readily polarized and have large remanent polarization value. Various pre-poling voltages (V_p) were applied to the top electrode of the PZT capacitors before H_2 annealing. When V_p was positive (0 ~ +6 V), the PZT films have a positive remanent polarization state (hereafter, $[+P_r]$ state) and when V_p was negative (0 ~ -6 V), they have a negative remanent polarization state (hereafter, $[-P_r]$ state). These pre-poled PZT capacitors were annealed in H_2(3 %)/N_2 gas system at 200 °C for 30 min and then their polarization characteristics were examined.

Figure 4(a) illustrates the P-E curves for Pt/PZT/Pt capacitors before and after H_2 annealing. The voltage shift (ΔE) of the curve is represented as $[(+E_c)+(-E_c)]/2$ where $+E_c$ and $-E_c$ are the positive and negative coercive field, respectively. For the $[+P_r]$ state PZT capacitor, the P-E curve shifted to the negative voltage direction by –

50 kV after H_2 annealing. For the PZT capacitor without pre-poling (V_p = 0 V), the curve also shifted to the negative direction by about –30 kV/cm. On the other hand, the curve shifted to the positive direction for the [-P_r] state PZT capacitor and the magnitude of the shift was about 30 kV/cm at V_p of –6 V. The degradation in saturation polarization ($2P_s$) by H_2 annealing was also affected by the pre-poling voltage. $2P_s$ is represented as $|+P_s|+|-P_s|$ where $+P_s$ and $-P_s$ are the positive and negative saturation polarization, respectively. The degree of the degradation in $2P_s$ for the [+P_r] state PZT capacitor was less than that of the capacitor without pre-poling. $2P_s$ of the [-P_r] state PZT capacitors decreased to be as much as the capacitor without pre-poling when low values of negative pre-poling voltages ($|V_p| \leq 4$ V) were applied, whereas the PZT capacitor pre-poled by V_p of –6 V showed less degradation than that without pre-poling.

The variation in hydrogen-induced degradation behavior with V_p is also found in ε_r-V characteristics as shown in Fig. 4(b). The hydrogen-induced degradation in ε_r of the pre-poled capacitors was less than that of the capacitor without pre-poling. The ε_r-V curves were shifted by H_2 annealing in the same direction as P-E curves. The curve for the capacitor without pre-poling exhibited the distinctive double peak after H_2 annealing. The double peak was found to disappear with increasing the magnitude of V_p. Since the peak position corresponds to the coercive voltage, the double peak in ε_r-V curve indicates that two different domain states coexist in the PZT film.

The effects of the PZT polarization state on the hydrogen-induced degradation behavior were studied as a function of H_2 annealing time at 200 °C. Figure 5 shows the dependences of $2P_s$ and ΔE on the annealing time for three kinds of capacitors: positively pre-poled, negatively pre-poled, and not pre-poled. All three capacitors exhibited similar tendency in $2P_s$ degradation with annealing time and were degraded severely within 10 min. However, the pre-poled capacitors were degraded less compared with the capacitor without pre-poling. The curve shifted toward negative at V_p = +6 V and toward positive at V_p = –6 V. When V_p = 0 V, the curve shifted toward negative, but the magnitude of voltage shift was smaller than when V_p = +6 V. It is noticeable that the magnitude of the voltage shift at V_p = 0 V became to reduce after 80 min.

Following mechanism is suggested for the hydrogen-induced degradation in order to explain the pre-poling effects. As mentioned previously, the degradation of Pt/PZT/Pt capacitor by H_2 annealing occurs due to oxygen vacancies that were created by hydrogen atoms dissociated from hydrogen molecules by the catalytic effect of Pt top electrode. The degradation behaviors were found to be different depending on polarization state of the PZT films before H_2 annealing. This implies

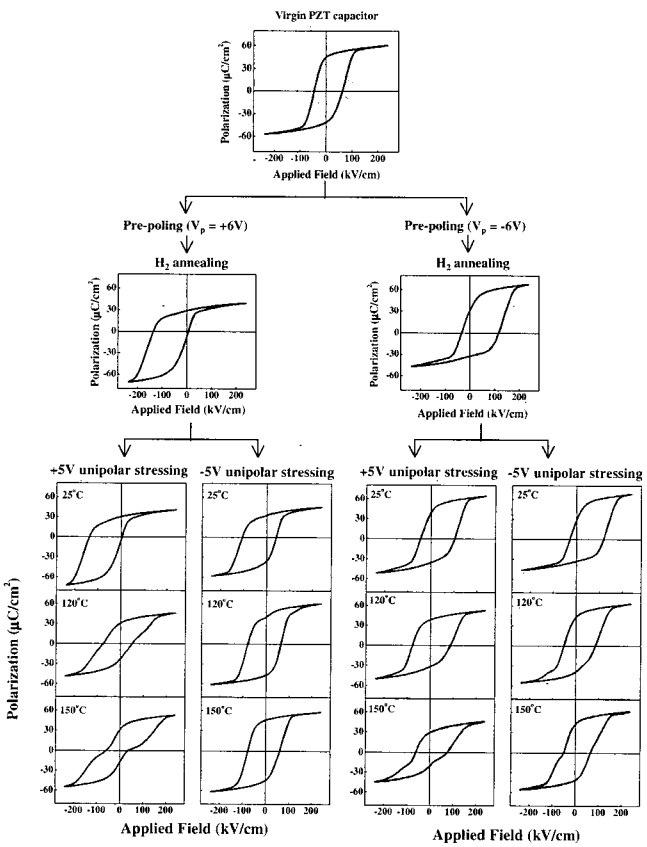

Fig. 6. Effects of unipolar stressing on the recovery characteristics of P-E curves for the degraded Pt/PZT(001)/Pt capacitors by annealing at various temperatures.

that the sources causing hydrogen-induced degradation must have a polarity. Therefore, it is thought that those causing the degradation of PZT capacitor are not hydrogen atoms but charged hydrogen ions. When ferroelectric thin films are annealed in the state of poling, voltage shift is induced by the trapping of charges in order to compensate the polarization charges in the interior of ferroelectric film, that is, to screen the depolarization field in the film[11,12]. A great number of hydrogen ions play a role in this compensation of polarization charges when ferroelectric film is annealed in the state of poling. For the [+P_r] state PZT ferroelectric film, positively charged hydrogen ions that diffuse from the Pt top electrode stay at the top electrode interface and provoke the formation of oxygen vacancies to compensate the polarization charges. In contrast, for the [-P_r] state PZT film, hydrogen ions diffuse toward bottom electrode interface and make oxygen vacancies form at the bottom. The voltage shift in P-E hysteresis curves appears by the internal field whose direction is dependent on the position of oxygen vacancies. For the [+P_r] state PZT films, negative voltage shift in P-E

curves appears after H_2 annealing because oxygen vacancies are mainly created at the top electrode interface. On the contrary, positive voltage shift in P-E curves appears for the [-P_r] state PZT films because oxygen vacancies are mainly created at the bottom electrode interface. The PZT film without pre-poling has random oriented domains and thus hydrogen ions can diffuse into the bulk of PZT films, resulting in severe degradation by the generation of oxygen vacancies inside the films. In the early stage of H_2 annealing, P-E curve shows negative voltage shift since hydrogen ions move from the top electrode interface toward the bottom. After H_2 annealing time is elapsed sufficiently, however, P-E curve becomes symmetric since oxygen vacancies are distributed through the PZT films. As shown in Fig. 5, the magnitude of voltage shift in P-E curve was reduced after 80 min.

The degradation of PZT capacitors induced by H_2 annealing can be recovered by post-annealing at elevated temperatures in oxygen environment since oxygen vacancies are removed by the introduction of oxygen from the outside environment. During the post-annealing process, electrical stressing may have an effect on the recovery behavior since the movement of charged elements such as oxygen vacancies can be affected by electric field. In this study, the recovery of the degraded PZT capacitors was examined by applying a unipolar pulse in oxygen environment. The PZT capacitors pre-poled by $V_p = \pm 6$ V were annealed in H_2(3 %)/N_2 gas system at 200 °C for 30 min. After H_2 annealing, unipolar pulse was applied to the top electrode with a frequency of 5 kHz, width 80 μsec and an amplitude of +5 V or –5 V at temperatures ranging from 25 °C to 150 °C. As shown in Fig. 6, when negative unipolar pulse was applied, the capacitors degraded by H_2 annealing recovered their polarization characteristics ($2P_s$ and $2P_r$) to original values with increasing temperature regardless of the polarity of the applied pulse. The P-E curve that had shifted by H_2 annealing was also recovered to be symmetric by post-annealing at high temperature when negative unipolar pulse was applied. However, when positive unipolar pulse was applied, the P-E curves were not effectively recovered by the post-annealing process.

When negative unipolar pulse is applied to the Pt/PZT/Pt capacitors that have been degraded by H_2 annealing, positively charged oxygen vacancies move toward top electrode and they are removed by the recombination with oxygen species supplied from outside environment, resulting in recovery of ferroelectricity and symmetry in P-E curve. The increase in post-annealing temperature causes the increase in the diffusion rate of incoming oxygen species and thus provoke the recovery of the degraded capacitors. However, positive unipolar stressing makes positively charged oxygen vacancies move toward the bottom electrodes. If incoming oxygen species exist in the form of negative ions, they cannot contribute to the recovery of polarization characteristics because of the difficulty in their migration to the interior of PZT films under positive electrical stressing.

4. CONCLUSION

Hydrogen atoms dissociated from hydrogen molecules by the catalytic effect of Pt top electrode penetrate into PZT films, and the penetrated hydrogen atoms generate oxygen vacancies by the reduction process of the PZT films, which is likely to cause severe degradation. The degree of degradation of the PZT capacitors and the direction of voltage shift in P-E curves induced by H_2 annealing was dependent on the polarity of pre-poling voltage. This implies that oxygen vacancies causing hydrogen-induced degradation are generated by hydrogen ions with polarity. The degraded ferroelectricity of the PZT films cannot be recovered simply by removing the hydrogen atoms from the PZT film. Recovery of the ferroelectricity is possible only by the supply of oxygen. The effects of unipolar electrical stressing on the recovery of the degraded Pt/PZT/Pt capacitors were investigated. For the negative unipolar stressing, the degraded ferroelectricity was recovered by eliminating oxygen vacancies by incoming oxygens at the top electrode interface, whereas the recovery of ferroelectricity was not so effective for the positive unipolar stressing.

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