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X-ray and Plasma Process Induced Damages to PLZT Capacitor Characteristics for DRAM Applications

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In this paper, the impacts of X-ray and plasma process-induced-damages to La doped Lead Zirconate Titanate (PLZT, $(Pb_{1-x}La_x)(Zr_{0.5}Ti_{0.5})O_3$) capacitor characteristics have been investigated from the viewpoint of gigabit scale dynamic random access memory (DRAM) applications Plasma damage causes asymmetric degradation on hysteresis characteristics of PLZT films. On the other hand, X-ray damage results in a symmetrical reduction of charge storage densities (Q_c's) for both polarities. As La concentration increases in the films, the radiation hardness of PLZT films on X-ray and plasma exposures is improved. It is observed that the damaged devices are fully recovered by thermal annealing under oxygen ambient.

Key words : PLZT, Ferroelectric capacitor, DRAM, Process-induced-damages

I. Introduction

Recently, high dielectric constant materials (such as $Pb(Zr,Ti)O_3$ (PZT), $(Pb,La)(Zr,Ti)O_3$ (PLZT) and $(Ba,Sr)TiO_3$ (BST)) have been extensively investigated as alternative dielectrics for gigabit generation DRAM (Dynamic Random Access Memory) capacitors because of their extremely small cell areas (< 0.25 μm^2).[1,2] The high dielectric constant materials should have excellent characteristics, such as high capacitance, low leakage current, good reliability and ease to fabricate thin films. At the same time, in order to realize the use of high dielectric constant materials for gigabit DRAM applications, the characteristics of the materials should not be degraded during post-deposition processes, such as patterning of stacked capacitor, deposition of intermetallic dielectric, and deposition and patterning of interconnection metals, and foaming gas annealing. Especially, the patterning process involves lithography and etching (either wet or dry etching) of the dielectrics and electrodes. X-ray as a lithography source may be employed for gigabit scale DRAM technology because of their high resolution.[3,4] At the same time, ULSI (Ultra-Large Scale Integration) DRAM technology requires several aniostrpic etching processes at post-capacitor processes in order to increase density of interconnection (such as metal, and contact or via). Therefore, the high dielectric constant material for DRAM capacitors must show strong hardness to radiation of X-ray and plasma. Even though issues on process damage are important in order to integrate high dielectric constant materials successfully in DRAM cells, few papers have been reported, and most of them have concentrated on the effects of the process damage on ferroelectrical properties for non-volatile RAM applications.[5-7]

In this paper, sol-gel derived 700 Å PLZT thin films have been used as test capacitor dielectrics, which are very promising materials for gigabit generation DRAM applications [1,8-10] The impact of X-ray and plasma process induced damages on PLZT film characteristics has been investigated from the viewpoint of gigabit generation DRAM applications. In this study, X-ray diffractometer and plasma asher were used in order to simplify the actual complicated X-ray lithography and dry etching processes. In addition, thermal annealing technique in oxygen ambient has been also suggested in order to recover the damaged properties.

II. Experimental Procedure

The test devices used in this study were MIM (metal-insulator-metal) capacitors. 250 Å thick Ti layer was deposited as a glue layer between Pt bottom electrode and SiO_2/Si substrate. The bottom electrode (1000 Å) was prepared by DC magnetron sputtering. The 700 Å PLZT (Zr/Ti=50/50) films were deposited using sol-gel method, and the PLZT solutions were prepared by anhydrous lead acetate ($Pb(OOCCH_3)_2$), lanthanum isopropoxide ($La(OCH(CH_3)_2)_3$), titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$), and zirconium n-butoxide butanol complex ($Zr(O(CH_2)_3CH_3)_4 \cdot C_4H_9OH$) precursors with methoxyethanol as a solvent. In this study, La concentration is defined as atomic ratio of La to Pb and the La concentration of the PLZT films ranges from 0% to 10%.[8-10] The crystallization anneal was done at 700°C for 30 minutes in O_2 ambient. Sputtered Pt (1000 Å) was also used as top electrode. The top electrodes with area of 32 μm × 32 μm were fabricated using wet etching technique. The fabricated MIM capacitors were then annealed in oxygen ambient at 650°C for 30 min. in order to relieve possible stress and damages generated during the capacitor process.

X-ray diffractometer (Rigaku, RU-200) and the plasma asher were used for simulating complicated X-ray lithography and dry etching systems, respectively. The fabricated 700 Å thick PLZT (0~10% La) test devices were exposed to a characteristic x-ray of Cu K_α (photon energy of 8 keV) for 2 hr. Tube voltage and current were 50 kV and 150 mA, respectively. This results in theoretical x-ray flux of 1.32×10^{12} quanta/cm^2·sec. The test devices received plasma damage in a ashing system with input power of 80 W in a pure nitrogen ambient for 2 min.

A modified Sawyer-Tower circuit was used to measure ferroelectrical hysteresis behaviors and charge storage density (Q_c'). Hewlett-Packard HP 8115A dual channel pulse generator supplied an input signal triangular pulse of 200 kHz. A 3.94 nF ceramic linear capacitor was used as a sense capacitor for the modified Sawyer-Tower circuit. Automation of measurement was made using HP Vectra personal computer connected to Tektronix DSA 602 digitizing signal analyzer and Tektronix TM5006A switch-matrix box. Additionally, HP 4285A precision LCR meter was used to obtain the small-signal high frequency capacitance of the high dielectric constant materials. Frequency of 200 kHz, step voltage of 0.1 V, and signal voltage of 50 mV were used. The leakage current measurement was performed using HP4140B pico-ammeter with step voltage of 0.05 V and step holding time of 1 sec.

III. Results and Discussion

It is reported that as La concentration increased from 0% to 10%, the charge storage density and leakage current of the PLZT capacitors were reduced and fatigue characteristics were improved.[8-10] Especially, 700 Å thick 5% La doped PZT capacitors show excellent characteristics for DRAM applications, having very high Q_c' (~100 μC/cm^2) with very low leakage (3×10^{-8} A/cm^2) at 1 V, which is the expected operating voltage for gigabit DRAM bipolar operation ($V_{DD}/2$).[8,11] Fig. 1 depicts the hysteresis loops of X-ray and plasma damaged devices compared with a hysteresis loop of a fresh device under 5 V bipolar operations. ±5 V operation results in the saturated loop of 700 Å fresh PLZT thin film. X-ray and plasma damaged devices exhibit different hysteresis loops compared to the fresh device of La 5% doped 700 Å thick PZT films (Fig. 1). The X-ray damaging process results in smaller DRAM polarization with maintaining a symmetric loop, though the plasma damage causes an asymmetric loop (negative polarization is much bigger than positive one). This asymmetry of hysteresis loops may indicate the existence of internal field in the plasma damaged devices.[12-14] Fig. 2 shows the charge storage density (Q_c') of 700 Å 5% PLZT films as a function of operating voltage with fresh and damaged devices. The fresh devices exhibit similar Q_c' for both polarities. For X-ray damaged devices, both $+Q_c'$ and $-Q_c'$ are decreased and no significant polarity dependence is observed. On the other hand, the plasma damaged device exhibits a drop of Q_c' for positive polarity, while negative Q_c' increases significantly. This may also indicate the presence of an internal field bias in the plasma damaged PLZT films.

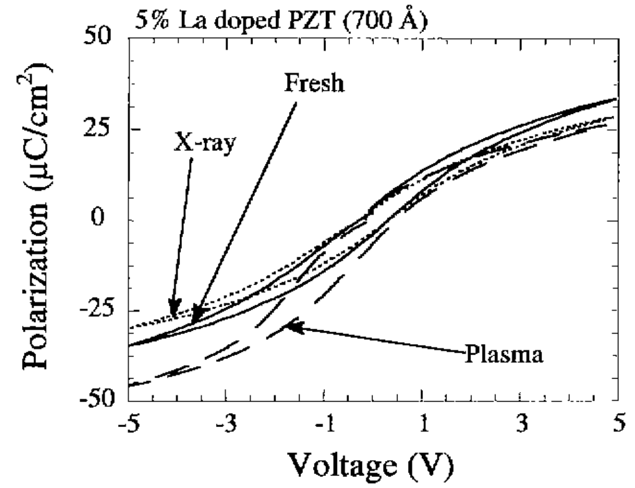

Fig. 1. Comparison of hysteresis loops between fresh and damaged devices by X-ray and plasma. 700 Å La 5% doped PLZT thin films were used

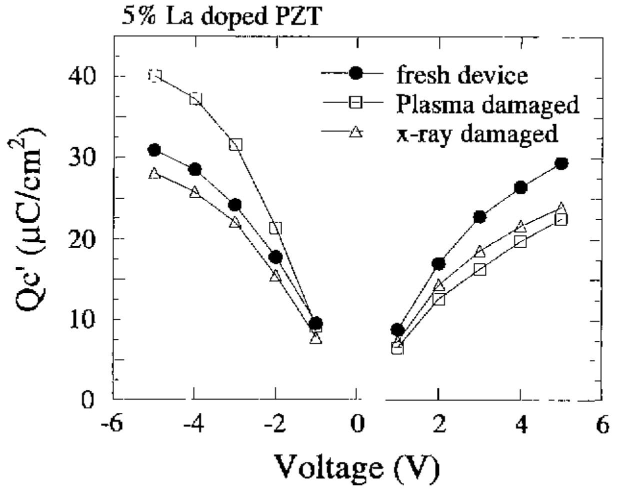

Fig. 2. Charge storage density (Q_c') as a function of operating voltage for fresh and damaged 700 Å PLZT (5%) thin films.

Fig. 3 depicts normalized Q_c' at 1 V as a function of La doping concentration for both polarities. Normalized Q_c' is defined as a ratio of Q_c' of the damaged device to that of the fresh device, which indicates that the value close to 1 is a better characteristic of the device. As La concentration increases, hardness to X-ray and plasma radiation is improved. This trend is similar to fatigue behavior of PLZT capacitors which is understood as results of domain pinning due to localized high electric field built by accumulation of space charge at domain or grain boundaries.[15,16] That is, the paraelectric phase (no domain effect involved) of PLZT films with high La concentration has better immunity from radiation damage because it is less sensitive to space charge effects. It is again observed that the x-ray process results in symmetrically degraded Q_c', whereas drastically asymmetric change in Q_c' (almost no variation of Q_c' for negative polarity, a drop of Q_c' for positive one), results from plasma damage (Fig. 3).

One of the basic differences between plasma and X-ray damage is that the incident species on the device are different; X-ray consists of photons with a wavelength of 1.54 Å, whereas plasma consists of electrons, neutral N atoms and charged nitrogen ions. Because x-rays can penetrate several microns (μm), it can generate excess space charges (such as, Pb^{2+} and Ti^{3+}, electron/hole pairs, and dangling bonds) throughout PLZT thin films, while plasma process affects only the region near the interface between bulk dielectrics and top electrode (Fig. 4).[16-18] It is not fully understood which species mainly cause the plasma damage effects. However, the plasma process may induce accumulation of negative space charges in PLZT near Pt top electrode. This results in a built-in internal field. On the other hand, X-ray damaged devices do not show a significant internal field due to uniformly distributed space charges. Due to induced space charges and internal field, the changes in the hysteresis loops of the damaged devices may occur. At the same time, damage processes causes similar effects on small-signal high frequency C-V curves (Fig. 5). Peak heights of the x-ray damaged device are reduced while maintaining a symmetry, whereas the plasma damage not only decreases capacitance, but also causes a shift of C-V curves to negative direction, which may indicate the existence of an internal field in the damaged devices. As a result, these damage processes give significant impacts on the polarization and capacitance characteristics.

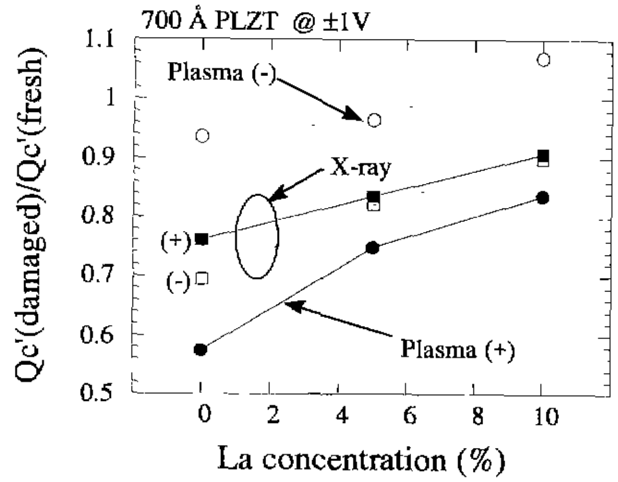

Fig. 3. Radiation hardness of Q_c' on X-ray and plasma exposures with various La concentrations.

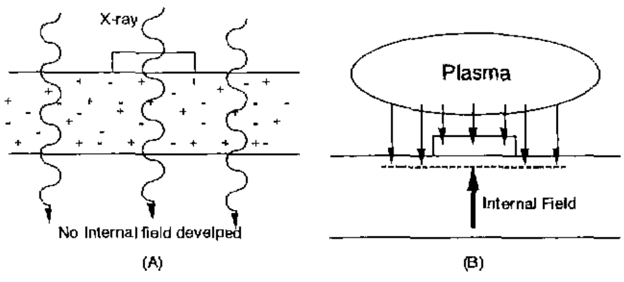

Fig. 4. Schematic diagram for (A) X-ray and (B) plasma damaging processes. Penetration depth of x-ray and plasma results in different degradation of Q_c'.

In addition, the damage processes affect leakage current behaviors (Fig. 6). X-ray damaged devices show less leakage current density than fresh devices. On the other hand, plasma damage results in an increase of leakage current possibly due to degradation of the Schottky interface between the top electrode and bulk PLZT resulting from heavy bombardment of electrons and nitrogen atoms and ions. It should be noted that

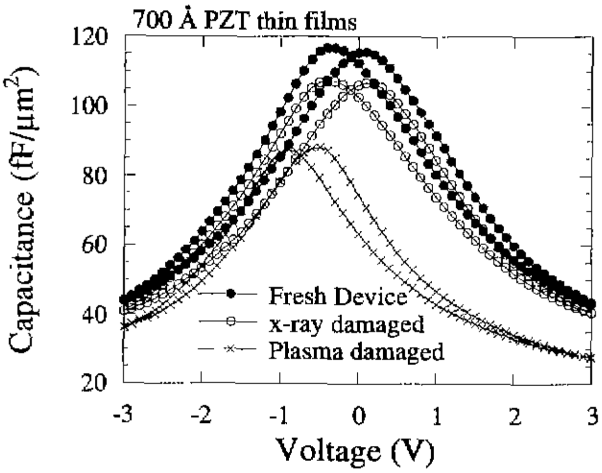

Fig. 5. High frequency C-V curves for fresh and damaged devices.

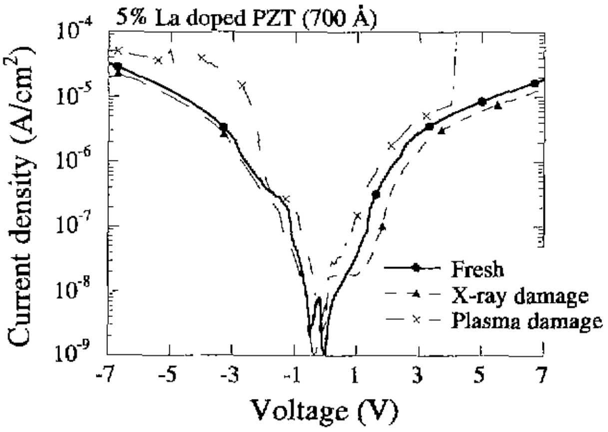

Fig. 6. Current density (J_L) as a function of voltage for fresh and damaged 700 Å 5% PLZT films.

the lowering of breakdown fields to the positive polarity (from 1.5 MV/cm to 0.6 MV/cm) results from the degradation of the interface during the plasma process. It is observed that films with different La concentrations shows similar degradation of breakdown fields to the positive polarity direction. For x-ray damaged films, it is not observed that breakdown fields are significantly decreased.

Without an external electric field, plasma damaged devices exhibit an aging phenomenon of Q_c'. On the other hand, X-ray damaged devices do not significantly vary the Q_c' for 17 days. In order to recover the characteristics of the damaged devices, a thermal annealing technique in oxygen ambient is used in this study. It is observed that thermal annealing even at 350°C results in symmetrical Q_c' for both polarities for plasma damaged devices. Higher temperature annealing up to 600°C increases Q_c' symmetrically, and annealing between 600°C and 750°C in O_2 ambient results in fully recovered characteristics. Annealing at above 800°C causes a reduction of Q_c' due to degradation of the top electrode and PZT film. High temperature annealing may cause thermal reactivation of the space charges (such as Pb^{3+} and Ti^{3+}) to normal electrical states (Pb^{2+}, Ti^{4+}).[18,19] Fig. 7 shows that Q_c's of both X-ray and plasma damaged devices are fully recovered after 650°C annealing in O_2 ambient for 30 min. Recovered films either from plasma or X-ray damage show almost the same charge storage densities as fresh devices. Recovery of leakage current and breakdown field of the plasma damaged devices are also observed.

The integration process also gives a significant effect on the fatigue behavior of damaged devices. As shown in Fig. 8, very asymmetric plasma damaged devices show anomalous fatigue behaviors; negative Q_c' drops very fast, while positive Q_c' reduces slowly. One may expect that Q_c's for both polarities meet after experiencing higher number of ±3 V stressing cycles. This indicates that the internal field of the damaged device is reduced. It is possibly because a redistribution of space charges induced by the plasma process occurs because of the external field applied on the device during fatigue experiments. Fatigue rate of the x-ray damaged devices is slower than the plasma damaged devices. It may be due to the nature of uniformly distributed space charges formed during the x-ray exposure. Fig. 9 shows almost identical fatigue behaviors between recovery-annealed and fresh devices. Since the fatigue behaviors of ferroelectric materials are closely related with space charge distributions, this implies that thermal recovery process results in the removal of excess space charges and internal fields induced by damage processes and healing of degraded interfaces.

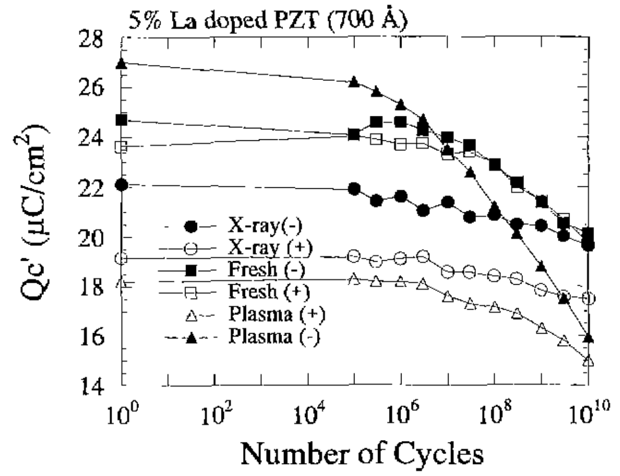

Fig. 8. Fatigue behaviors for fresh and damaged devices under ±3 V bipolar stressing. Open and dark marks indicate Q_c' of positive and negative polarities, respectively.

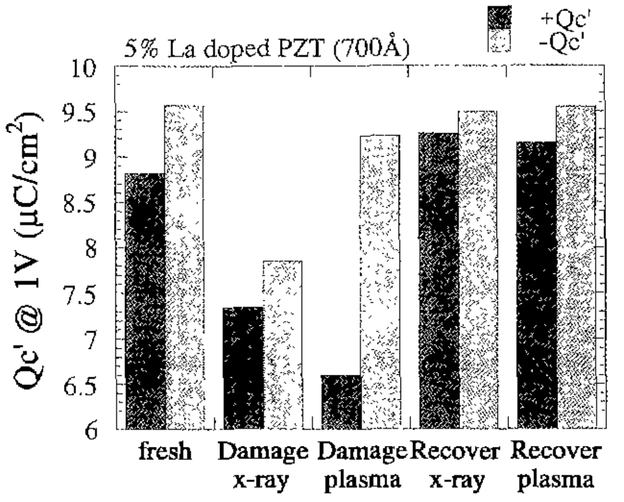

Fig. 7. The effect of recovery annealing on Q_c' at 1 V for 700 Å 5% PLZT films. Recovery annealing was performed at 650°C, in a pure oxygen ambient, for 30 min.

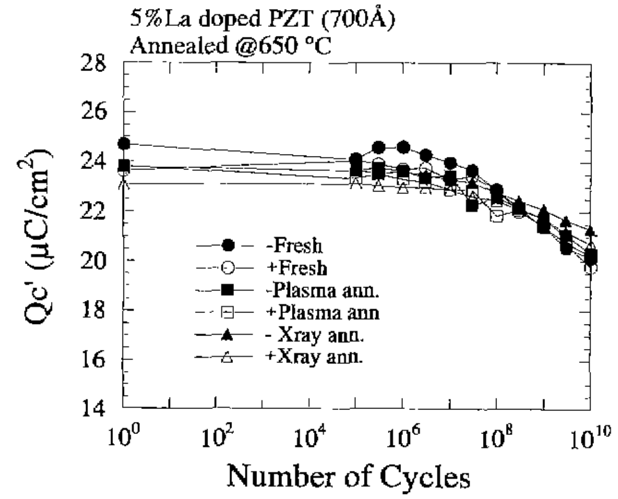

Fig. 9. Fatigue behaviors for the fresh device and the devices recovered from process damage. Q_c' is obtained with 3 V operation under accelerated ±3 V bipolar stressing.

IV. Conclusions

In this paper, the impacts of x-ray and plasma process-induced-damages to PLZT capacitor characteristics have been investigated from the viewpoint of gigabit generation DRAM applications. X-ray damages result in symmetric hysteresis loops, while plasma damages cause asymmetric hysteresis loops of PLZT films. The x-ray damaged devices exhibit a reduction of charge storage densities for both polarities, whereas plasma damaged devices shows asymmetric polarization ($+Q_c' < -Q_c'$). Furthermore, the plasma process causes an increase in leakage current and a degradation of breakdown field for positive polarity. As La concentration increases in the films, the hardness of PLZT films on x-ray and plasma is improved. Thermal annealing gives a recovery from damaged properties. Annealing at 650°C in a pure oxygen ambient for 30 min. causes recovery of the electrical properties (such as, charge storage density and fatigue behaviors) of 700 Å 5% La doped PZT films.

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