

## Degradation of PLZT Capacitors at Elevated Temperature in Deuterium Gas

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Deuterium gas treatment of ferroelectric (Pb,La)(Zr,Ti)O<sub>3</sub> [PLZT] thin film capacitors with a top electrode of IrO<sub>2</sub> and bottom electrode of Pt showed significant polarization loss when baked at 200 °C at a pressure of 5 Torr. The degradation of the capacitors was attributed to the reduction of the IrO<sub>2</sub> top electrode to Ir, absorption/dissociation of D<sub>2</sub> on the Ir and diffusion of atomic deuterium into the PLZT film. The concentration of D in the PLZT film was on the order of 10<sup>19</sup> atoms/cm<sup>3</sup> and this concentration level was sufficient to degrade the ferroelectric properties of the capacitors by inhibiting domain switching. In addition, SIMS profiles indicated that the D<sub>2</sub> gas was also diffusing through the PLZT film and dissociating on Pt bottom electrode. The dissociation of the D<sub>2</sub> gas and diffusion into the PLZT film was attributed to the catalytic properties of Ir and Pt. These results indicate that minimizing the capacitors exposure to hydrogen containing ambient at elevated temperature is necessary for ensuring ferroelectric capacitor reliability.

Key words: deuterium, PLZT, capacitors, SIMS, ferroelectric domains

### 1. INTRODUCTION

Ferroelectric capacitors are being developed worldwide for use in ferroelectric random-access memory [FRAM<sup>1</sup>]. Pb(Zr,Ti)O<sub>3</sub> [PZT] is the most popular FRAM capacitor material because of its high remnant polarization and processing temperatures that are compatible with conventional CMOS devices.

Recently, asymmetrical capacitors with top and bottom electrodes of different materials such as IrO<sub>2</sub> as the top electrode and with Pt bottom electrodes has gained wide-spread acceptance among FRAM manufacturers<sup>2</sup>. The Pt which is (111) oriented, forms a template for growth of (111) oriented PZT and the IrO<sub>2</sub> top electrode shows good fatigue endurance to repeated bi-polar pulses used in FRAM operation. This type of capacitor also has shown high reliability.

In order to take advantage of FRAM capacitor's low voltage operation and high speed, the FRAM capacitor must be integrated with transistors, interlayer metals and dielectrics used in CMOS processing. Typical deposition of the interlayer materials is done in a hydrogen or water vapor containing gas ambient at elevated temperature. Pt and Ir are known catalysts for the dissociation of H<sub>2</sub> into atomic hydrogen and are widely used in chemical processing industry. However, Pb in contrast is a known as a metal catalyst poison and its impact on the Pt electrode catalytic nature until recently was unclear.

Problems associated with H<sub>2</sub> degradation of PZT capacitors and poor reliability with Pt top electrode has been identified previously<sup>3</sup>, but the degradation mechanism for capacitors with top electrode IrO<sub>2</sub> was only recently clarified by using D<sub>2</sub> gas<sup>4</sup>. D<sub>2</sub> gas has similar properties of H<sub>2</sub> but deuterium is easier to quantify than hydrogen analytically using secondary ion mass spectroscopy (SIMS). In addition, it has been shown that the Pt film underneath the PLZT film is catalytically active<sup>5</sup>. As a result, degradation of PLZT capacitors may take place at both interfaces. In this paper, results are summarized describing the degradation of PLZT capacitors in D<sub>2</sub> gas focusing on the electrodes.

### 2. EXPERIMENTAL

PLZT films doped with La, Ca and Sr (abbreviated PLZT) were sputtered to a thickness of 200 nm from a ceramic target onto sputter-deposited Pt (175 nm) /Ti (20 nm) electrodes on top of SiO<sub>2</sub>/Si(100) wafers. The PLZT film was then annealed briefly at 600°C and 750°C for crystallization. The PLZT films had a (111) orientation as measured by X-ray diffraction. The top electrode of IrO<sub>2</sub> 200 nm thick was reactively sputter deposited at room temperature from an iridium metal target, and then the capacitor top electrodes were patterned and reactively ion-etched. Finally, the capacitor was annealed in an oxygen atmosphere at 650°C for 60 min.

Degradation of the capacitors and PLZT film (see Fig. 1) was carried out at 200°C in flowing 3% D<sub>2</sub>/N<sub>2</sub> gas at 5 torr in a tube furnace. Electrical measurements were made on 200x200 μm<sup>2</sup> and 50x50 μm<sup>2</sup> IrO<sub>2</sub> reactively-ion-etched top electrodes using a Radiant Technologies (New Mexico, USA) RT6000HVS-5 ferroelectric tester for hysteresis measurements at 3V, where the bias voltage was applied to the bottom electrode. Thermal desorption spectroscopy (TDS) was carried out on a 10x10 mm sample in a ESCO Ltd. (Musashino, Japan) EMD-1000 with a heating rate of 1°C/sec from room temperature to 700°C. SIMS analysis was used to measure the D- (amu 2) concentration and <sup>18</sup>O relative concentration using a quadrupole mass spectrometer detector of the IrO<sub>2</sub> top electrode before and after D<sub>2</sub> gas annealing. The SIMS of the capacitor was performed with a Cs primary beam and the concentration of D was determined by measurement of PLZT implanted with a known concentration of D (Charles Evans Assoc., California, USA). Auger electron spectroscopy

(AES) of the surface of the  $\text{IrO}_2$  top electrode was analyzed to determine the O and Ir surface concentration (Fujitsu Analysis Lab., Kawasaki, Japan).

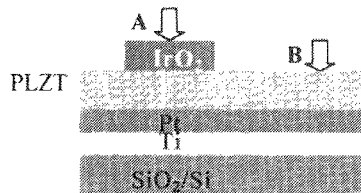


Fig. 1 Schematic of sample used for hysteresis measurements and  $\text{D}_2$  gas treatment evaluation. The arrows indicate locations of SIMS analysis and these points are identified as A and B.

### 3. RESULTS AND DISCUSSION

#### 3.1 $\text{D}_2$ baking impact on PLZT

To better understand the source of the degradation of PLZT films, films with two different structures consisting of  $\text{IrO}_2/\text{PLZT}/\text{Pt}$  (A site) and  $\text{PLZT}/\text{Pt}$  (B site) were baked in  $\text{D}_2$  gas at  $200^\circ\text{C}$  (Fig 1) and analyzed by SIMS. The initial concentration of D in the PLZT films before  $\text{D}_2$  baking was below the SIMS detection limit of  $1\text{e}17$  atom/ $\text{cm}^2$ . After baking the sample for 10 min the concentration of D underneath the  $\text{IrO}_2$  was still low but the concentration in the PLZT was  $8\text{e}18$  atom/ $\text{cm}^3$  (Fig. 2). Further baking of the sample and SIMS analysis revealed that the D concentration increases at both locations but the largest increase in D concentration is observed underneath the  $\text{IrO}_2$ .

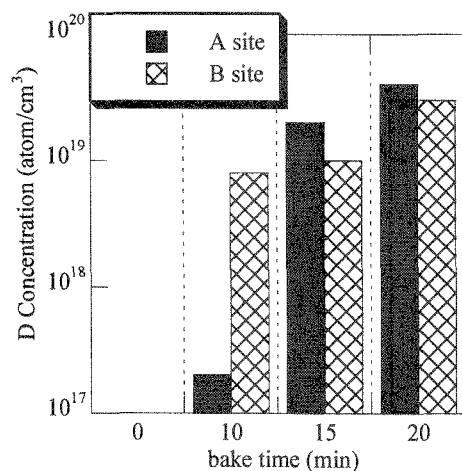


Fig. 2 D concentration in PLZT film at sites A and B versus  $200^\circ\text{C}$   $\text{D}_2$  gas bake time.

A noticeable difference in the  $\text{IrO}_2$  surface morphology was observed as a result of the  $\text{D}_2$  gas baking. The  $\text{D}_2$  baking resulted in a drastic change in the  $\text{IrO}_2$  film roughness when compared to the initial state versus the capacitor after 20 min in  $\text{D}_2$  gas<sup>4</sup> (Fig 3). The TEM cross-sectional images revealed deep voids within the  $\text{IrO}_2$  film. Additional characterization by Auger

electron spectroscopy revealed that the  $\text{IrO}_2$  was reduced to Ir metal. It should be noted there is no observable physical change in the PLZT film before and after  $\text{D}_2$  baking under these conditions.

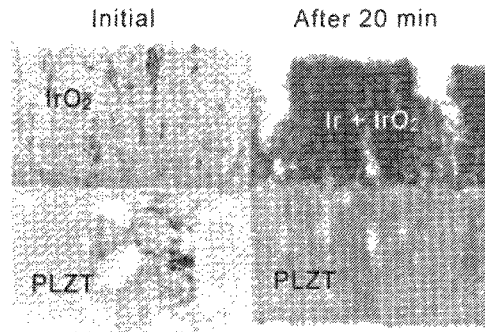
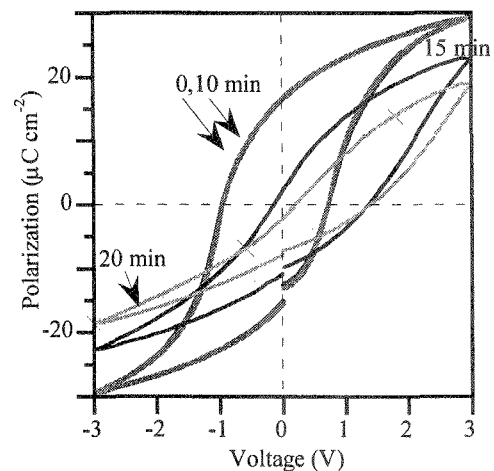


Fig 3. TEM cross-sectional images of  $\text{IrO}_2/\text{PLZT}$  before and after baking in  $\text{D}_2$  gas for 20 min ( $1\text{cm} = 110\text{nm}$ ).

#### 3.2 Ferroelectric Properties

Measurement of the hysteresis properties of the capacitors (A) revealed a degraded hysteresis loop with a reduction in the remnant polarization (Fig 4) and the hysteresis loop was shifted to the right, which is an indication of the positive charge at the  $\text{IrO}_2/\text{PLZT}$  interface. The loop shift to the right increased and reduction in the remnant polarization increased with



baking time.

Fig. 4 Hysteresis loops of capacitors as a function of  $\text{D}_2$  bake time shown initially, after 10, 15 and 20 min in  $\text{D}_2$  gas at  $200^\circ\text{C}$ .

Previously, the loss of ferroelectricity as indicated by the degradation of the hysteresis loop has been attributed to space charge within the PZT film<sup>6</sup>. Hydrogen within the titanate perovskites has been noted to be accommodated as an interstitial donor defect<sup>7</sup>. Charge concentrations on the level of  $1\text{e}19$  atom/ $\text{cm}^3$  and higher has been calculated to cause the degradation of hysteresis loop of PZT capacitors. Therefore, the result shown here are in agreement with those reported in the literature. The degradation of the loop and direction of the loop shift is dependent upon the charge location within the PLZT film. Another source of degradation of

the capacitor is the potential loss of oxygen due to reduction of the PLZT film by D<sub>2</sub> gas.

3.3 TDS results and degradation mechanism

Analysis of the thermal desorption spectroscopy for the sample before and after D<sub>2</sub> gas baking revealed the deuterium contain species within the PLZT film. TDS results showed several peaks intensities at AMU 3, 4, 19, 20 and 32, which correspond to HD, D<sub>2</sub>, DHO, D<sub>2</sub>O and O<sub>2</sub>, respectively. (There is a high background signal at mass 19 at 20 which corresponds to F+ and Ar++, respectively.)

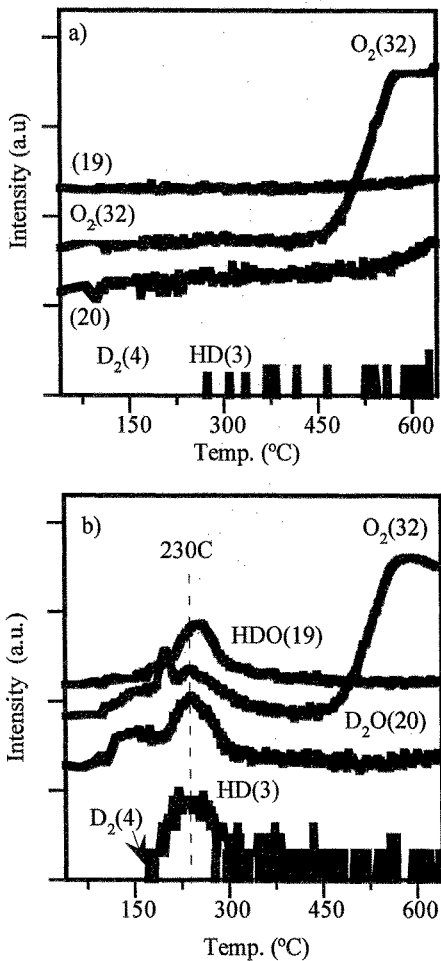


Fig 4. a) TDS spectra of a 1x1 cm<sup>2</sup> sample depicted in Fig 1 before D<sub>2</sub> baking and b) TDS spectra of sample after D<sub>2</sub> baking for 20 minutes.

The TDS results particularly indicate the desorption of D containing species such as HD, HDO and D<sub>2</sub>O occurred at temperatures between 100 and 300°C. The results were summarized in Fig. 5. The amu peak at 20, shows two peaks indicating desorption of absorbed species at the surface at 140°C and a larger peak at 230°C which was attributed to D in the PLZT film. These results indicate that the dissociated D is penetrating into the PLZT film and bonding with lattice oxygen in the PLZT. This mechanism has been proposed previously by

Aggrawal<sup>8</sup> for hydrogen degradation of PZT films. Concerning the hydrogen observed in the TDS results, it is attributed to OH in the PLZT film and PLZT grain boundaries. Although H is present in the PLZT film as hydrocarbons and OH, the majority of H appears to be primarily electrically inactive. Based upon the above TDS results, at elevated temperature the interstitial deuterium can also reduce the film by bonding with another hydrogen or deuterium atom to form water and then desorbing at high temperature. The desorption of water then would lower the oxygen content of the PLZT film. This mechanism has been suggested previously<sup>3</sup> but this reduction mechanism does not account for the high concentration of deuterium in the PLZT and its impact on the electrical properties observed in Figs 2 and 3.

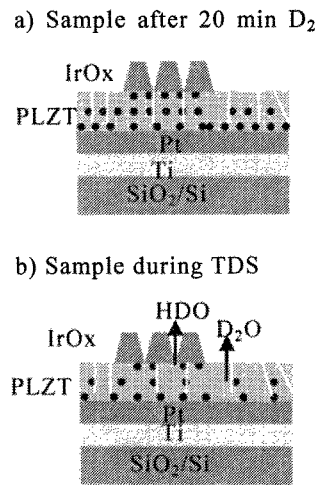
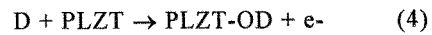
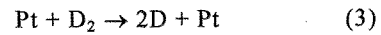
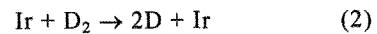
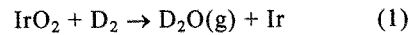


Fig. 5 Schematic of sample after D<sub>2</sub> baking and during TDS where, • represents D atoms in the PLZT film.

Therefore, it is proposed that the overall mechanism of deuterium interaction with the capacitor electrodes and PLZT film degradation is summarized in four equations for the capacitor as well as the PLZT film.



The mechanism is similar to what was proposed previously,<sup>4</sup> but it incorporates deuterium dissociation on Pt interface as well as from the Ir metal which was reduced from the IrO<sub>2</sub> top electrode. In the case of the capacitors with IrO<sub>2</sub> top electrode, D<sub>2</sub> dissociation on Pt does not occur until after the IrO<sub>2</sub> is reduced and voids are formed in the IrOx film allowing for D<sub>2</sub> diffusion through the IrOx and PLZT to the Pt surface. This explains why after 10 minutes of baking in D<sub>2</sub> gas, very little D<sub>2</sub> is observed in the PLZT capacitor (A) whereas the D concentration in the PLZT film (B) is nearly 1e19 atoms/cm<sup>3</sup> (Fig. 2). Thus, it appears that the IrO<sub>2</sub> film

initially acts as a sacrificial barrier to inhibit  $D_2$  diffusion into the capacitor. In the case of PLZT films without the  $IrO_2$  film,  $D_2$  is thought to diffuse through the PLZT grain boundaries and then dissociate on Pt and D then back diffuses into the PLZT grains and bonds with interstitial oxygen in the PLZT lattice. Because Pb is a catalytic poison and previous results showed that the Pt was oxidized,<sup>3</sup> until now it was hypothesized that the Pt was catalytically inactive. However, the results shown above indicate that the Pt film has catalytically active sites beneath the PLZT film. This same type of Pt catalytic activity has been shown previously with  $(Ba,Sr)TiO_3$  film on Pt<sup>9</sup>, indicating that the Pt is catalytically active even when covered by another material.

The degradation of the PLZT capacitor is attributed to interstitial D as has been proposed previously for hydrogen degradation of PZT<sup>8</sup>. In this case, the deuterium bonds with apical oxygen ions to form a polar deutroxil ion<sup>8</sup> which inhibit switching of the Zr, Ti atoms in the lattice. From these results it is apparent that since hydrogen is present in many processes during FRAM integration, in order to ensure high reliability, it is essential to reduce the exposure of the Pt in the bottom electrode to hydrogen containing ambient.

#### 4. CONCLUSION

The degradation of the capacitor polarization was attributed to the reduction of the  $IrO_2$  top electrode to Ir, absorption/dissociation of  $D_2$  on the Ir and diffusion of deuterium into the PLZT film. In addition, the Pt bottom electrode was catalytically active and contributed to  $D_2$  dissociation into D at the Pt/PLZT interface. The concentration of D in the PLZT film was on the order of  $10^{19}$  atoms/cm<sup>3</sup> in the capacitors and was sufficient to degrade the ferroelectric properties. The dissociation of the  $D_2$  gas and diffusion into the PLZT film was attributed to the catalytic properties of Ir and Pt and inhibited domains from switching. These results indicate that keeping the capacitors away from hydrogen containing ambient is necessary for ensuring ferroelectric capacitor reliability in FRAM.

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