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IrO₂/Pb(Zr,Ti)O₃/Pt Capacitor Degradation with D₂ Gas at Elevated Temperature

Jeffrey S. CROSS^{*}, Yoshimasa HORII¹, Naomi MIZUTA, Satoru WATANABE and Takeshi ESHITA¹

Fujitsu Laboratories Ltd., 10-1 Morinosato-Wakamiya, Atsugi, Kanagawa, 243-0197, Japan

¹Fujitsu Limited, 10-1 Morinosato-Wakamiya, Atsugi, Kanagawa, 243-0197, Japan

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The degradation of Pb(Zr,Ti)O₃ [PZT] ferroelectric capacitors with IrO₂ top electrode and Pt bottom electrode was evaluated by baking at 200°C in 3% D_2/N_2 gas at 4.5 Torr up to 20 min. The polarization of the capacitor decreased by more than 60% and the hysteresis loop shifted to positive side when baked for 15 min or more in D_2/N_2 gas. Auger Electron Spectroscopy indicated that the surface of the IrO₂ was reduced to Ir metal during D_2 baking. Secondary ion mass-spectroscopy (SIMS) of the PZT capacitor revealed that the degraded PZT contained a D concentration of 5 × 19 atoms/cm³. The degradation of the capacitor followed a three step mechanism: 1) reduction of the IrO₂ top electrode surface to Ir, 2) Deuterium dissociation into to D+ ions on the Ir surface and 3) diffusion of D+ into the PZT film. [DOI: 10.1143/JJAP.41.698]

KEYWORDS: hydrogen, SIMS, diffusion, PZT, deuterium, degradation

1. Introduction

Ferroelectric thin films are currently being developed worldwide because of their application in low voltage, non-volatile random access memories (FRAM).¹⁾ Pb(Zr,Ti)O₃ [PZT] is one of the most widely used ferroelectric materials because of its high remnant polarization and it is currently being used in a number of commercially available products.²⁾

Ferroelectric capacitors typically incorporate noble metals or their oxides such as Pt and IrO_2 as electrodes because of their high temperature stability. However, both Pt and Ir are catalytically active materials for the dissociation of H₂. During the integration of the ferroelectric capacitor into a semiconductor device, the capacitor is exposed to gases containing hydrogen at elevated temperature, which degrade the capacitor. Over the past 5 years, a number of papers have been published on the hydrogen degradation of PZT capacitors but there is some debate as to whether the degradation mechanism occurs at the electrode/PZT interfacial^{3,4)} or is a PZT film phenomena.⁵⁾

One of the challenges in understanding the degradation mechanism has been to identify where the hydrogen is located within the capacitor after H₂ treatment. Although H can be measured and quantified by secondary ion-mass spectroscopy (SIMS),^{6,7)} there is a high H background in the capacitor due to absorbed H₂O, OH and hydrocarbons as well as H₂ gas in the SIMS chamber. Studying the PZT degradation using D₂ gas is much easier, because D can be easily quantified by SIMS because there is a little D background signal in PZT and also a very low SIMS instrumental background level. D₂ gas treatment at elevated temperature causes dielectric degradation of (Ba,Sr)TiO3 capacitors with Pt electrodes.^{8,9} In addition, D₂ gas treatment of Si based transistors has shown to improve device lifetime compared to transistors passivated in hydrogen gas.¹⁰⁾ Therefore, D₂ gas treatment of PZT is both interesting from a research point of view as well as practical from a device manufacturing standpoint.

To our knowledge, D_2 gas degradation of PZT capacitors has not been presented previously in the literature. This study was undertaken to examine the degradation of doped PZT capacitors with IrO_2 top electrode and Pt bottom electrodes in order to propose a degradation mechanism and relate it to space charge in the film.

2. Experimental Method

200 nm thick PZT films doped with La, Ca and Sr (abbreviated PZT¹¹) with excess Pb were sputtered onto sputter-deposited Pt (175 nm)/Ti (20 nm) electrodes on SiO₂/ Si wafers. The PZT film was then annealed briefly at 600°C and 750°C to crystallize it. The top electrode of IrO₂ (200 nm) was reactively sputter deposited at room temperature, 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 was carried out at 200°C in flowing 3% D_2/N_2 gas or 3% H_2/N_2 at 4.5 Torr in a tube furnace. Electrical measurements were made on $200 \times$ $200\,\mu\text{m}^2$ and $50 \times 50\,\mu\text{m}^2$ IrO₂ etched top electrodes using a Radiant RT6000HVS-5 ferroelectric tester using both pulses to determine the average switching polarization, Q_{sw} , and hysteresis measurements at 3 V. The bias voltage was applied to the bottom electrode. The leakage current of the capacitors was measured with a HP 4140A pAmp meter. The leakage bias voltage was applied to bottom electrode and ramped from 0 to 10 volts with steps of 0.25 V and a hold time of 1s. Secondary ion mass spectroscopy (SIMS) analysis was used to measure the D-(amu 2) concentration and ¹⁸O relative concentration using a quadrapole mass spectrometer detector of a patterned capacitor 200× $200 \,\mu m^2$ IrO₂ top electrode before and after D₂ gas annealing. The SIMS of the capacitor was performed with a Cs primary beam and the concentration of D was determined by measurement of PZT implanted with a known concentration of D (Charles Evans Assoc., California, USA). Rutherford back-scattering was performed on the IrO₂ films to determine the O/Ir ratio (Charles Evans Assoc., California, USA). Auger electron spectroscopy (AES) of the surface of the IrO₂ top electrode was analyzed to determine the Ir, O and Pb surface concentration (Fujitsu Analysis Lab., Kawasaki, Japan). Thermal desorption spectroscopy (TDS) was preformed on a $1 \times 1 \text{ cm}^2$ sample of the patterned PZT capacitors at a heating rate of 1°C/s from room temperature to 750°C to measure desorbed gas relative concentrations.

^{*}E-mail address: jscross@flab.fujitsu.co.jp



Fig. 1. Switchable polarization of PZT capacitors versus 200°C baking time in 3% H_2 and 3% D_2 gas measured at 3 V.

3. Results and Discussion

Degradation of the PZT capacitors was evaluated in both H_2 and D_2 gas atmospheres at 200°C. The degradation results show that the capacitors exhibit little change in polarization at 10 min but then a sharp decrease in polarization was observed at 15 min and further loss at 20 min (Fig. 1). Annealing the capacitor in H_2 gas lead to slightly more degradation than the D_2 gas at equivalent times. These results indicate that the degradation of the capacitor with D_2 gas is similar to H_2 gas, but H which is lighter diffuses more quickly by a factor of $2^{1/2}$ (ref. 12) and results in greater loss in the polarization than D_2 .

AES and SEM of the IrO_2 electrode surface revealed both a chemical change in the composition and surface topography resulting from the D_2 gas anneal. Initially, the surface of the IrO_2 top electrode shows a fine-grained structure before the D_2 annealing [Fig. 2(a)]. After annealing the capacitor in D_2 gas for 15 min, the surface of the IrO_2 is reduced to Ir metal as confirmed by AES and voids appear due to the oxygen loss resulting in surface roughening [Fig. 2(b)].

The presence of Pb on surface of the IrO_2 top electrode was confirmed by AES. Previously, it has been reported that Pb on the surface of IrO_x retards the degradation of the PZT capacitor since Pb is a known catalyst poison and Pb is a catalytically inactive metal.⁴⁾ The capacitor degradation reported here occurred more rapidly at lower temperature than that previously reported since we evaluated the degradation at low pressure, 4.5 Torr, in order to reduce the partial pressure of oxygen in annealing chamber. The oxidation state of Ir is dependent on the oxygen partial pressure particularly at elevated temperatures.¹³⁾

The reduction of IrO_2 top electrode was clearly indicated by SIMS profiles of the ¹⁸O intensity (Fig. 3) taken thru the top electrode into the PZT film. The SIMS profiles show initially the ¹⁸O profile was constant within the IrO_2 film and



(a)



Fig. 2. SEM photographs of the surface of IrO_x surface (a) before and (b) after baking for 15 min in 3% D₂ gas.



Fig. 3. SIMS relative ^{18}O profile in the IrO₂ electrode and top portion PZT film versus D₂ gas baking time.

the oxygen concentration decreased at the surface as the D_2 gas baking time increased from 10 to 20 min. The SIMS results indicate that the roughened surface of the IrO_2 film was reduced and the reduced region extends further into the top electrode as the baking time increased. Due to electrode surface roughening, the interface between the top electrode and PZT became broader with bake times of 15 and 20 min. It should be noted that the ¹⁸O signal appears to increase in PZT film but this was an artifact of the SIMS measurement due to ionization yield differences, matrix effects and charging.¹⁴

SIMS analysis of the PZT capacitor showed the D concentration in the PZT increased as D_2 baking time increased (Fig. 4). SIMS analysis of the capacitor before D_2 annealing showed that the concentration of D in the PZT was below the detection limit of the instrument 7×10^{16} atoms cm⁻³. There was a slight increase in the D concentration above the background at 10 min with the concentration greatly increasing throughout the PZT film after baking at 15 and 20 min.

A comparison of the amount of D in the PZT and switchable polarization, Q_{sw} , is shown in Table I. The average concentration of D in the capacitor was 5×10^{19} atoms cm⁻³ after annealing for 15 min and increased further to 7×10^{19} atoms cm⁻³ after annealing for 20 min. Correspondingly the polarization of the capacitor decreased



Fig. 4. SIMS D concentration profiles in PZT for different D_2 gas baking times.

Table I. Result of PZT capacitor D_2 annealing time and D concentration versus 3 V measured V_c and Q_{sw} .

Anneal time (min)	D Conc. (at cm^{-3})	$V_{\rm c}$ Ave (V)	$Q_{\rm sw}~(\mu{\rm Ccm^{-2}})$
0	$< 8 \times 10^{16}$	-0.10	30
10	2×10^{17}	-0.10	29
15	5×10^{19}	0.5	9
20	7×10^{19}	0.6	5

Note: V_c Ave = $[+V_c + (-V_c)]/2$ from hysteresis loop.

as the deuterium concentration in the capacitor increased (Table I). Although D concentration increased with baking time, the capacitor leakage current showed only a slight increase when measured at 3 V.

The simplified mechanism of the capacitor degradation is illustrated in Fig. 5 and thought to occur sequentially in the following steps based upon the above results:

$$IrO_2 + D_2 \to D_2O + Ir \tag{1}$$

$$Ir + D_2 \rightarrow 2D + Ir$$
 (2)

$$D + PZT \rightarrow PZT - D$$
 (3)

These results indicate that the IrO_2 top electrode initially acts as a barrier to the degradation while it is being reduced or consumed and then the Ir metal subsequently catalyzes the PZT degradation by dissociation the D_2 into ions as indicated by eqns. (1) and (2). The D⁺ then diffuses into the PZT lattice via the top electrode and through the PZT grain boundaries. Therefore, the IrO_2 top electrode may be thought of as a "consumable barrier layer/electrode". The D within the PZT film probably occupied sites within the PZT lattice as well as at the PZT grain boundaries. The D absorbed on the PZT grain boundaries was thought to have little impact on the ferroelectric properties.

Previously, it has been shown that H₂ gas annealed PZT capacitors with a Pt top electrode show O-H bonding by Raman spectroscopy indicating that the H is actually located within the PZT perovskite lattice.⁵⁾ The hydrogen bonded to O then inhibits the dipole switching of the Zr^{+4} or Ti^{+4} atoms in the lattice. In this study, we were unable to observe the O-D bonds by Raman spectroscopy probably due to the low concentration of D in the PZT film, which was below the Raman detection limit of several atomic percent. TDS analysis of the $20 \min D_2$ gas annealed PZT capacitors showed significant peaks at AMU 19 and 20 when heated above 220°C, indicating the evolution of HDO and D₂O into the gas phase, respectively. The TDS results also indicate that the D radicals that diffuse into the PZT are bonding with O in the lattice and out gassing at temperatures above $150^{\circ}C.^{15)}$

Simulations of the PZT capacitor hysteresis loops as a function of negative space concentration has recently shown that space charge within the PZT film reduces the both the coercive voltage (V_c) and P_r .¹⁶) The reduction in PZT capacitor Q_{sw} and relative charge concentration are both in agreement with simulation results of Baudry.¹⁶)

As mentioned previously, there has been considerable debate upon the nature of hydrogen degradation of PZT capacitors. Shimamoto reported that the degradation of the capacitor is due to the interfacial reduction of the PZT-top electrode interface.³⁾ Although interfacial reduction may occur, we cannot concur that interfacial reduction is degrading the ferroelectric properties of the capacitor. Instead, we propose that the degradation is due to incorporation of D+ into the PZT lattice and forming O–D bonds, where the D inhibits the switching as proposed previously for H degradation of PZT by Aggarwal.⁵⁾ Based upon the positive voltage shifted hysteresis loops (Table I), a charge gradient exists in the D₂ baked PZT capacitors, which is in agreement with results of Kanaya.⁶⁾ Kanaya observed a positive shift in the hysteresis loop indicating



Fig. 5. Model of the IrO₂/PZT/Pt capacitor D₂ degradation process.

positive charge at the top interface after annealing the PZT capacitor in a hydrogenous atmosphere. The source of positive charge at the capacitor top interface can be attributed to either oxygen vacancies or D incorporation into the film.⁸⁾ We believe that the positively shifted hysteresis loop observed after D₂ gas baking (see Table I), is due to an asymetrical D concentration gradient in the PZT film (Fig. 5).

4. Conclusion

In summary, we demonstrated that the D₂ gas degrades PZT capacitors similar to hydrogen gas baking, which resulted in a loss of polarization. The degraded PZT capacitors showed a roughened IrO_x top electrode surface and loss of oxygen. Metallic Ir on the top electrode was catalytically active which dissociated the D₂ into ions which then diffused into the PZT. SIMS analysis indicated that the D₂ gas baked PZT capacitors had a D concentration of 5×10^{19} to 7×10^{19} atoms cm⁻³ when baked for 15 and 20 min, respectively. The loss of capacitor switching polarization was attributed to O–D bonds in the PZT lattice.

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1) FRAM is a registered trademark of Ramtron International Corporation,

Colorado, USA.

- Fujitsu Limited Electronic Devices homepage, http://edevice.fujitsu. com/, click on FRAM.
- Y. Shimamoto, K. Kushida-Abdelghafar, H. Miki and Y. Fujisaki: Appl. Phys. Lett. 70 (1997) 3096.
- K. Kushida-Abdelghafar, M. Hiratani and Y. Fujisaki: J. Appl. Phys. 85 (1999) 1069.
- S. Aggarwal, S. R. Perusse, C. W. Tipton, R. Ramesh, H. D. Drew, T. Venkatesan, D. B. Romero, V. B. Podobedov and A. Weber: Appl. Phys. Lett. **73** (1998) 1973.
- H. Kanaya, T. Iwamoto, Y. Takahagi, I. Kunishima and S. Tanaka: Integrat. Ferroelectr. 25 (1999) 235.
- H. Ashida, M. Tomotani, T. Tamura, K. Matsuura, Y. Goto and S. Otani: Integrat. Ferroelectr. 21 (1998) 97.
- J. D. Baniecki, R. B. Laibowitz, T. M. Shaw, C. Parks, J. Lian, H. Xu and Q. Y. Ma: J. Appl. Phys. 89 (2001) 2873.
- J.-H. Ahn, P. C. McIntyre, L. Wills Mirkarimi, S. R. Gilbert, J. Amano and M. Schulberg: Appl. Phys. Lett. 77 (2000) 1378.
- J. W. Lyding, K. Hess and I. C. Kizilyalli: Appl. Phys. Lett. 68 (1996) 2526.
- 11) T. D. Hadnagy and T. Davenport: Integrat. Ferroelectr. 22 (1998) 183.
- 12) D. Kek and N. Bonanos: Solid State Ionics 125 (1999) 345.
- 13) M. Peuckert: Surf. Sci. 144 (1984) 451.
- 14) The actual D concentration at the electrode/PZT/electrode interfaces and the SIMS measured D concentration may differ for several different reasons. Particularly, the rough top electrode surface may underestimate the D near the top electrode interface due interface broadening and then possibly overestimate the D concentration near the bottom interface due to sample charging and D movement in PZT during SIMS analysis. See http://www.cea.com/cai/simstheo/charging.htm. Also see P.C. McIntyre, J. H. Ahn, R. J. Becker, R.-V. Wang S. R. Gilbert, L. Wills Mirkarimi and M. T. Schulberg: J. Appl. Phys. **89** (2001) 6378.
- 15) J. S. Cross, Y. Horii, N. Mizuta, S. Watanabe and T. Eshita: presented at 12th Int. Symp. Integrated Ferroelectrics, March, 2001, Colorado Springs, CO, USA.
- 16) L. Baudry: J. Appl. Phys. 86 (1999) 1096.