Effects of Heterostructure Electrodes on the Reliability of Ferroelectric PZT Thin Films

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(Received March 15, 2002; Accepted April 8, 2002)

ABSTRACT

The effect of the Pt electrode and the Pt-IrO$_2$ hybrid electrode on the performance of ferroelectric device was investigated. The modified Pt thin films with non-columnar structure significantly reduced the oxidation of TiN diffusion barrier layer, which rendered it possible to incorporate the simple stacked structure of Pt/TiN/poly-Si plug. When a Pt-IrO$_2$ hybrid electrode is applied, PZT thin film properties are influenced by the thickness and the partial coverage of the electrode layers. The optimized Pt-IrO$_2$ hybrid electrode significantly enhanced the fatigue properties with minimal leakage current.

Key words : Pt, TiN, Pt-IrO$_2$ hybrid electrode, Fatigue, PZT

1. Introduction

For successful preparation of ferroelectric and high-dielectric devices, we may separate the requirements imposed on the electrodes in at least two categories: The first requirement is imposed by the integration of the perovskite materials with Si based devices, that is, improving the oxidation resistance of conventional barrier materials, such as TiN or TiAlN, through microstructure densification and modification of electrodes. And the second requirement is imposed by the effects of the electrodes on the electrical properties of the ferroelectric capacitors. The latter is especially critical for ferroelectric capacitors to be used for non-volatile ferroelectric memories(NVFeRAMs) since the electrodes can significantly affect the electrical properties such as fatigue, imprint, and leakage current of the capacitors based on perovskite thin films.[1-4]

The present paper will report the effects of the microstructural modification of noble metal, especially platinum electrodes, on the oxidation behavior of the underlying TiN diffusion barrier layer for the first category. In an approach to address the second category issues, we have performed an extensive series of experiments on PZT thin films with Pt-IrO$_2$ hybrid electrode layer. Detailed ferroelectric properties involving this system will be discussed here.

2. Experimental

Ferroelectric PZT thin films(Zr:Ti = 35:65) were prepared using Chemical Solution Deposition(CSD). Films were spin coated at 4000 rpm for 30 seconds and subsequently dried

at 450°C for 10 min and 650°C for 2 min for each layer. After two layers were deposited, the coated films were annealed at 650°C for 30 min in a furnace through direct insertion. Final film thickness was 250 nm measured by Scanning Electron Microscopy(SEM). For the microstructure modification of Pt electrode, we performed multi-step sputtering process, which was performed in inert(Ar) ambient for the first step and the third step and in mixed Ar/O$_2$ or Ar/N$_2$ for the second step. TiN was used for underlying diffusion barrier. For hybrid electrodes, thin IrO$_2$ was reactively deposited to three different nominal thickness, 6, 15 or 30 nm, by sputter deposition. Crystallinity, microstructure, leakage current, P-E hysteresis and fatigue characteristics of the films were investigated using X-Ray Diffraction(XRD), Field Emission Scanning Electron Microscopy(FESEM), cross-sectional Transmission Electron Microscopy(TEM), programmable electrometer(Keithley 617) and a ferroelectric tester(RT 6000S, Radiant), respectively.

3. Results and Discussion

Fig. 1 shows cross-sectional TEM images of our modified Pt/TiN films. As-deposited modified Pt film shows non-columnar structure(Fig. 1(a)). It is well known that TiN film underneath conventional columnar Pt is severely oxidized around 500-550°C post-annealing process, which is caused by the diffusion of oxygen along the grain boundaries of the Pt film.[5] However, TiN with our modified non-columnar Pt film does not show the oxidation behavior even after 650°C post-annealing process as shown in Fig. 1(b). Generally, the grain size of columnar Pt thin films on TiN is approximately equal to the film thickness.[5] In other words, if the thickness or grain size of Pt can be increased, oxidation rate will be
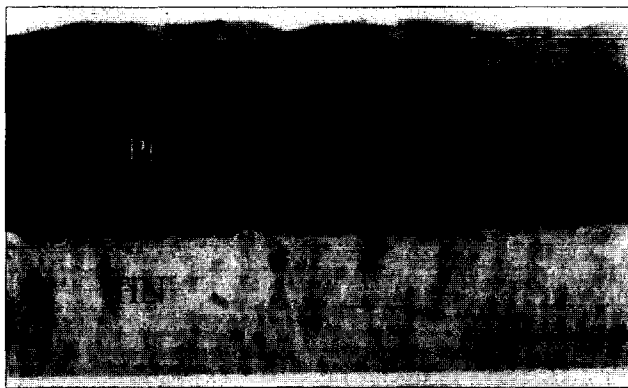
(a)
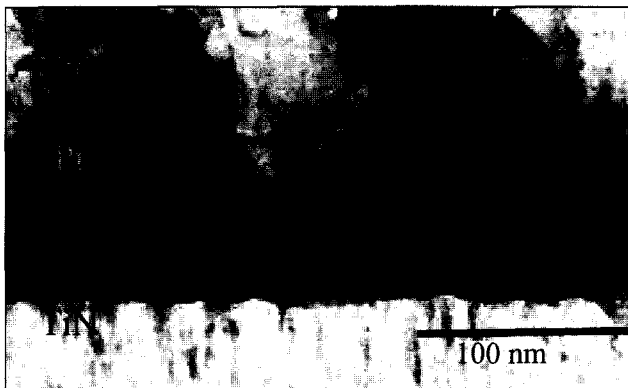
(b)

Fig. 1. TEM images of modified Pt films (a) as -deposited and (b) after 650°C annealing process.
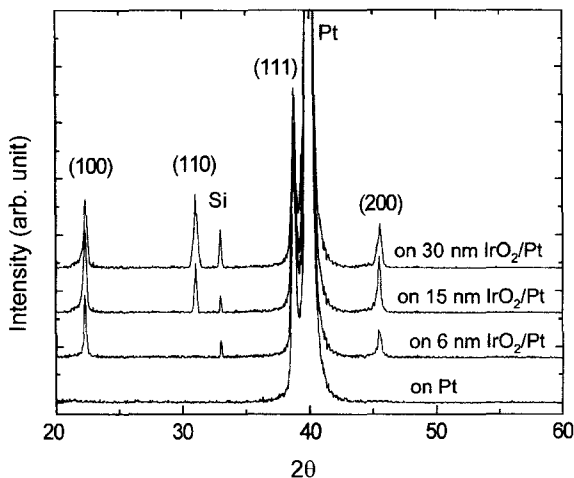

Fig. 2. XRD patterns of the PZT (Zr:Ti = 35:65) thin films grown on IrO_2/Pt hybrid electrodes having different IrO_2 inter-layer thickness from 0 to 30 nm.

Fig. 2 shows the XRD patterns of the PZT thin films as a function of IrO_2 thickness on Pt. The PZT thin film directly on (111) oriented Pt shows highly textured (111) orientation because the activation energy for nucleation of PZT is the lowest for heterogeneous nucleation on lattice matched substrates.[6-8] The film on 6 nm IrO_2/Pt shows some (100) orientation, but has a strong (111) preferred orientation, while the film on thicker IrO_2/Pt reveals random orientation. In general, nucleation and cryastallization of a single phase perovskite PZT film is much more difficult to achieve on oxide electrode than on Pt. In addition, it is well known that PZT films on oxide electrode tend to have a large amount of non-ferroelectric second phase and to display a rosette microstructure.[8] Kwok and Desu[9] reported that whenever
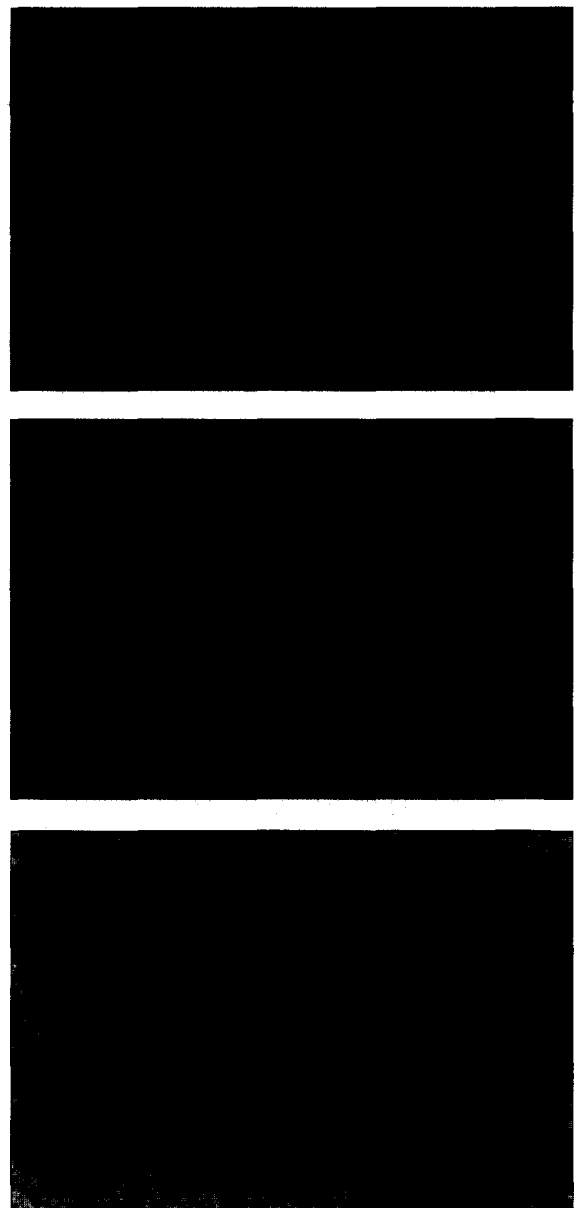
decreased due to the increase of diffusion path. Possible way to retard the oxidation rate is the microstructure modification from columnar structure to granular structure of Pt, since non-columnar grain structure has longer diffusion path as compared to columnar structure of Pt film. This result is well matched with above hypothesis.

Fig. 3. FESEM micrographs of the PZT film surfaces having IrO_2 bottom-layers with the thickness of (a) 0 nm, (b) 10 nm and (c) 30 nm, respectively.

pyrochlore intermediate phase was formed, the pyrochlore to perovskite conversion occurred through an interface controlled transformation and the resultant films were randomly oriented. For a consistent trend, XRD patterns of PZT films grown on IrO$_2$ show less textured orientation shown in fig. 2 even if second phase of PZT is not detected by XRD due to its nano-scale grain size.

Fig. 3 shows the FESEM micrographs of the PZT film surfaces having IrO$_2$ bottom-layers with thickness of (a) 0 nm,

(b) 10 nm and (c) 30 nm, respectively. The figures clearly show a more non-uniform and rosette-like surface morphology with increasing bottom-IrO$_2$ layer thickness confirming the XRD results. As shown in Fig. 3, the PZT film on Pt consists of a fine grained structure. In contrast, films on 30 nm IrO$_2$/Pt have a rosette structure implying existence of perovskite islands in a pyrochlore matrix.

Fig. 4(a) and (b) show J-V curves of PZT thin films as a function of IrO$_2$ thickness in the bottom and top hybrid elec-
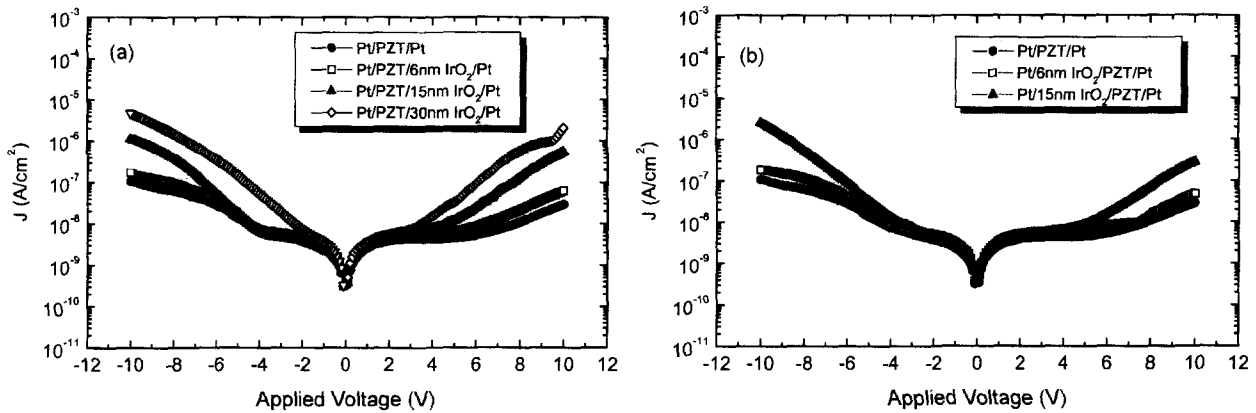

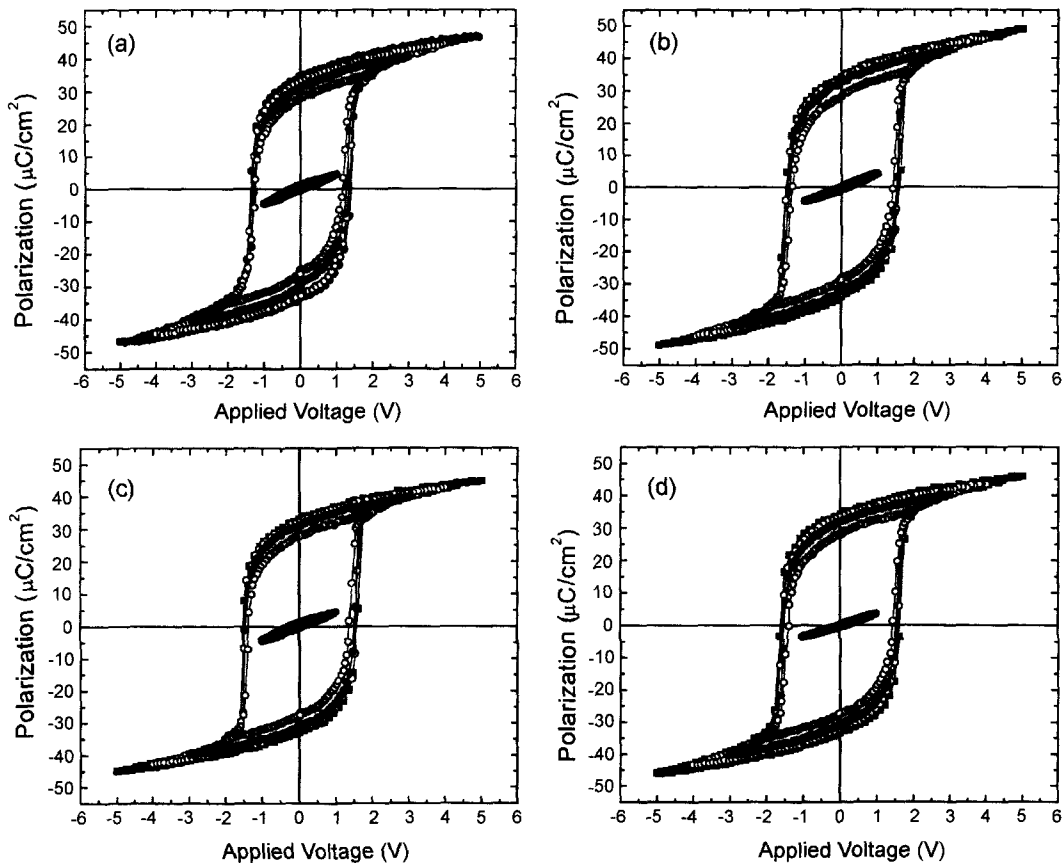Fig. 4. J-V curves of PZT thin films as a function of (a) bottom IrO$_2$ and (b) top IrO$_2$ hybrid electrode thickness.

Fig. 5. P-V hysteresis loops of PZT films with four different electrode stacks (a) Pt/PZT/Pt, (b) Pt top/6 nm IrO$_2$/PZT/Pt, (c) Pt/PZT/6 nm IrO$_2$/Pt bottom and (d) Pt top/6 nm IrO$_2$/PZT/6 nm IrO$_2$/Pt bottom as a function of maximum applied voltage from 1 V to 5 V.

trode, respectively. PZT thin films on Pt and 6 nm IrO_2/Pt hybrid electrode show excellent leakage current density, which is in the order of 10^{-7}–10^{-8} A/cm^2 up to 10 V, while the films on thicker IrO_2 (15 nm and 30 nm) bottom hybrid electrode reveal higher leakage current density(10^{-5}–10^{-6} A/cm^2). The trend of leakage current density of the PZT films as a function of IrO_2 top hybrid electrode thickness is nearly same when applying same bias conditions as shown in Fig. 4(b).

In general, PZT on oxide electrode has two known pyrochlore-type second phases.[8,9] The first is insulating PZT pyrochlore($Pb_2(Zr,Ti)_2O_{7-x}$). However, this type of pyrochlore would not cause high leakage currents, because it has a high resistivity of about 10^{10} or 10^{11} Ω-cm. The second pyrochlore-type phase is PZT pyrochlore-related conducting phase(specifically for RuO_2, PZT pyrochlore-ruthenate ($Pb_2(Ru,Zr,Ti)_2O_{7-x}$) or lead ruthenate($Pb_2Ru_2O_{7-x}$)). This would be a high conduction path and its lattice constant is very similar to PZT pyrochlore. It is, therefore, more likely that these phases are responsible for the high leakage current of the PZT films on oxide electrode/Pt hybrid structures. This is consistent in that the films on thicker IrO_2/Pt would produce much more PZT pyrochlore-related conducting phase. We surmise that PZT pyrochlore or PbO is more reactive with IrO_2 than it is with PZT perovskite and therefore forms conducting phase very easily like the case of RuO_2. Based on above results and hypothesis, we decide that the optimum thickness of IrO_2 hybrid top and/or bottom electrode is below 10 nm(specifically, 6 nm in this paper).

Fig. 5 shows P-V hysteresis loops of PZT films with four different electrode stacks(Pt/PZT/Pt, Pt/6 nm IrO_2 top/PZT/Pt, Pt/PZT/6 nm IrO_2/Pt bottom and Pt/6 nm IrO_2 top/PZT/6 nm IrO_2/Pt bottom) as a function of applied voltage from 1 V to 5 V. It is observed that the loop shapes for the films on the four different electrode stacks are almost same, while the remanent polarization(P_r) values are slightly different. Up to 6 nm IrO_2 insertion, the measured P_r values of the PZT thin films are similar(35 ~ 38 µC/cm^2 at 5 V), regard-

less of electrode structures. However, the PZT thin films grown on thick IrO_2/Pt hybrid bottom electrode reveal much smaller P_r value(20 ~ 25 µC/cm^2 at 5 V) as compared to the films with Pt or 6 nm IrO_2/Pt electrode as shown in Fig. 6. The data presented above are entirely consistent with the fact that the P_r values of the PZT films depend on the film orientation and microstructure, which in turn appear to be substantially affected by the thickness of hybrid bottom electrode. Other possible factors which can affect the polarization behavior of PZT capacitors include the presence of second phases or locally inhomogeneous crystallization of the PZT films as shown in Fig. 3.

Fig. 7 shows fatigue properties of the PZT thin films with four different electrode stacks. When performing fatigue cycles with 5 V and 500 kHz squared wave pulse, the Pt/
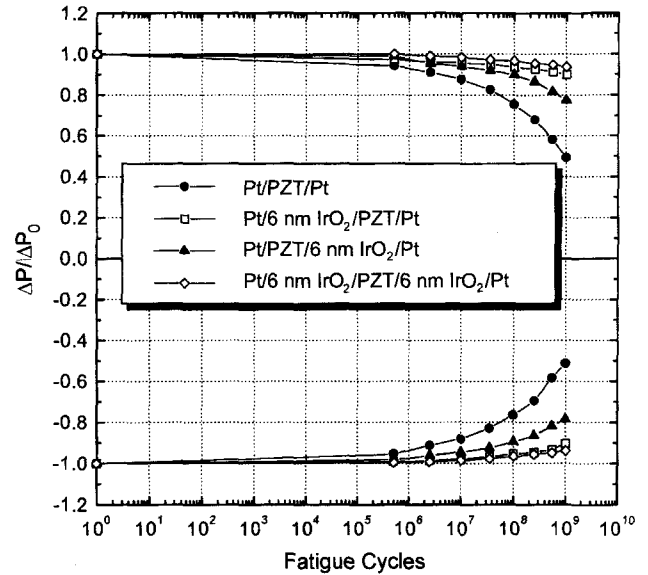

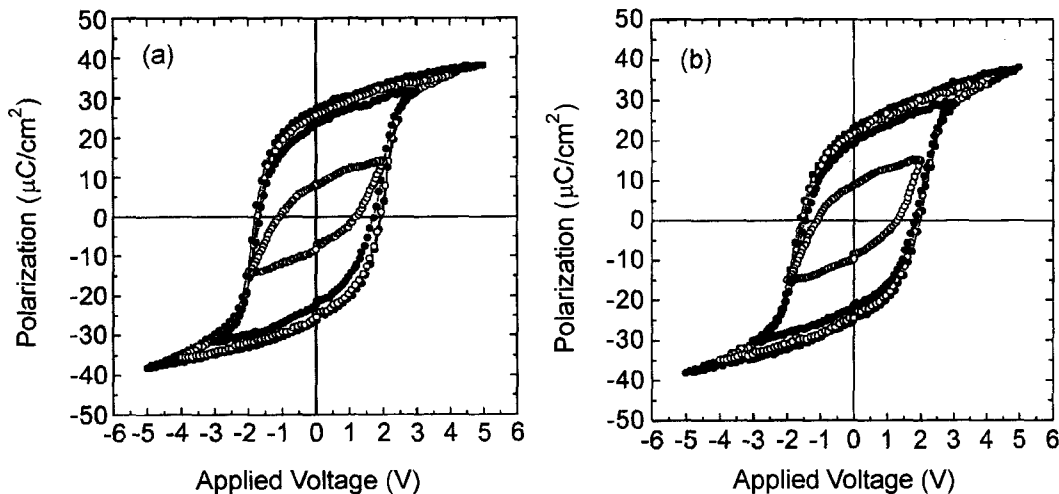**Fig. 7.** Normalized fatigue properties of the PZT thin films with four different electrode stacks.

Fig. 6. P-V hysteresis loops of PZT thin films with (a) Pt/PZT/15 nm IrO_2/Pt bottom, (b) Pt/PZT/30 nm IrO_2/Pt bottom as a function of maximum applied voltage from 2 V to 5 V.

PZT/Pt capacitors show an abrupt polarization decrease between 10^7 and 10^9 cycles as expected, whereas PZT with both top and bottom 6 nm IrO_2/Pt hybrid electrodes exhibit an almost flat fatigue profile up to 10^9 cycles. It has been shown by many researchers that fatigue of PZT thin films can be substantially alleviated by use of conductive oxide such as RuO_2, IrO_2, $SrRuO_3$ or hybrid electrodes, incorporated only in both top and bottom electrodes.[10,11] However, our results indicate that high polarization endurance behavior with fatigue cycles can be obtained even on asymmetrical Pt/6 nm IrO_2/PZT/Pt capacitors as shown in Fig. 7. Recently similar results have been presented for asymmetrical top Pt/SrRuO_3/PLZT/Pt by Stolichinov et al.[12] They suggested that fatigue of switching polarization of PZT film capacitors is controlled by the interfaces and the most probable fatigue mechanism is related to the inhibition of the near-interfacial nucleation of the opposite domains by the entrapped mobile carriers. This suggestion is well matched to our results presented above. However, our asymmetric hybrid bottom electrode result indicates another features for fatigue behavior that the use of only bottom 6 nm IrO_2/Pt is less effective in improving the fatigue resistance of PZT than that of top 6 nm IrO_2/Pt hybrid electrode. This result imply that another strong dependence of fatigue rate on electrode material for PZT thin films may be due to the effect of the accumulation of oxygen vacancies near the film/electrode interface during fatigue cycling. Accumulation of oxygen vacancies would tend to stabilize the trapped charge near the film/electrode interface, which could reduce the local detrapping rate, potentially promoting fatigue. In general, the oxide electrode materials can act as a sink for oxygen vacancies and they might reduce the accumulation of oxygen vacancies near the film/electrode interface. A reduced accumulation of oxygen vacancies near the interface might reduce the electronic charge trapping and consequently lead to less domain wall pinning and better fatigue properties. If this is the case, top electrode/film interface is much more important than bottom electrode/film interface since the source of oxygen vacancy is volatilized PbO and this kind of PbO out-diffusion to the top electrode creates much more vacancies near the top interface than near the bottom interface.

4. Conclusion

The reliable ferroelectric devices impose stringent requirement on the electrode materials, since the electrical properties and device performance can be significantly affected by the electrodes used with ferroelectric thin films. The microstructure modification of Pt electrode with non-columnar structure significantly reduced the oxidation of TiN diffusion barrier layer, which made it possible to incorporate the simple stacked structure of Pt/TiN/poly-Si plug. The right combination of Pt-IrO_2 hybrid electrode showed drastically improved fatigue and other ferroelectric properties of the PZT capacitors.

Acknowledgement

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