

강유전체 PZT 박막의 신뢰도에 미치는 헤테로구조 전극의 영향에 대한 연구

論 文

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

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Abstract - The effect of the Pt electrode and the Pt-IrO₂ 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-IrO₂ hybrid electrode is applied, PZT thin film properties are influenced by the thickness and the partial coverage of the electrode layers. The optimized Pt-IrO₂ hybrid electrode significantly enhanced the fatigue properties of the PZT thin film with minimal leakage current.

Key Words : Pt, TiN, Pt-IrO₂ 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 nonvolatile ferroelectric memories(NVFeRAMs) since the electrode 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-IrO₂ 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) method. The films were spin coated at 4000rpm for 30 seconds and subsequently dried at 450°C for 10min and 650°C for 2min for each layer. After two layers were deposited, the coated films were annealed at 650°C for 30min in a furnace through direct insertion. Final film thickness measured by Scanning Electron Microscopy(SEM) was 250nm. 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/O₂ or Ar/N₂ for the second step. TiN was used for underlying diffusion barrier. For hybrid electrodes, thin IrO₂ was reactively deposited to three different nominal thickness, 6, 15 or 30nm by sputter deposition, respectively. 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.

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3. Results and Discussion

Fig. 1 shows cross-sectional TEM images of modified Pt/TiN films. As-deposited modified Pt film shows non-columnar structure in 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 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.

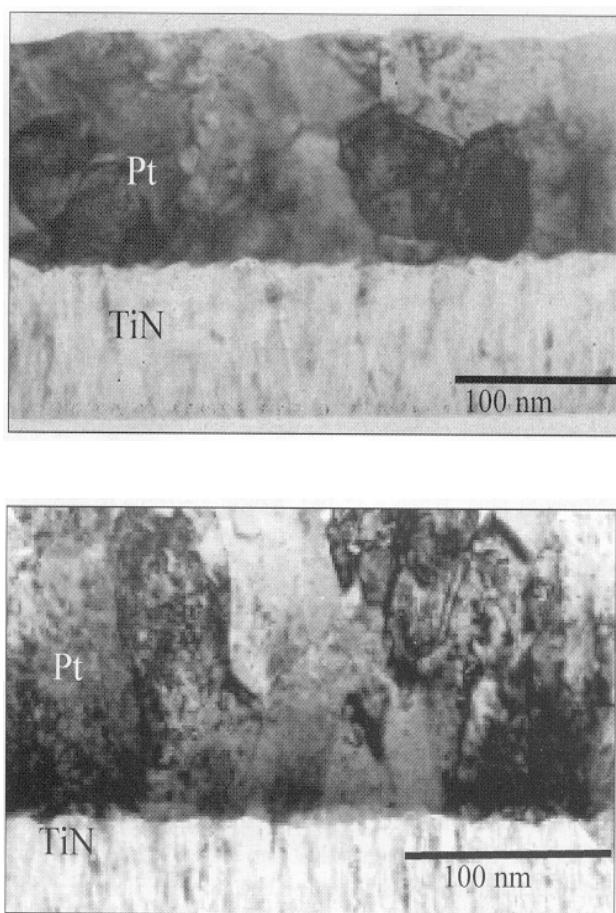


Fig. 1 TEM images of modified Pt (a) as-deposited and (b) after 650°C annealing process.

Fig. 2 shows the XRD patterns of the PZT thin films as a function of IrO₂ 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 6nm IrO₂/Pt shows some (100) orientation, but has a strong (111) preferred orientation, while the film on thicker IrO₂/Pt reveals random orientation. In general, nucleation and crystallization 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 Desu⁹⁾ reported that whenever 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 IrO₂ show less textured orientation shown in Fig. 2 even if second phase of PZT is not detected by XRD due to its nano-scale grains size.

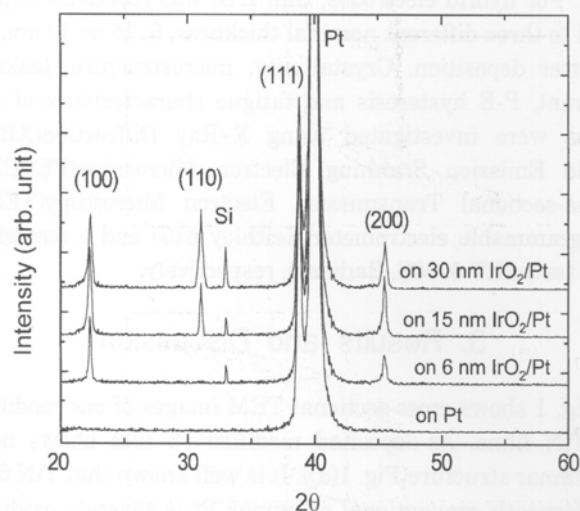


Fig. 2 XRD patterns of the PZT (Zr:Ti=35:65) thin films grown on IrO₂/Pt hybrid electrodes having different IrO₂ inter-layer thickness from 0 to 30nm.

Fig. 3 shows the FESEM micrographs of the PZT film surfaces having IrO₂ bottom-layers with thickness of (a) 0nm, (b) 10nm and (c) 30nm, respectively. The figures clearly show a more non-uniform and rosette-like surface morphology with increasing bottom-IrO₂ layer thickness confirming the XRD results. As shown in Fig. 3, the

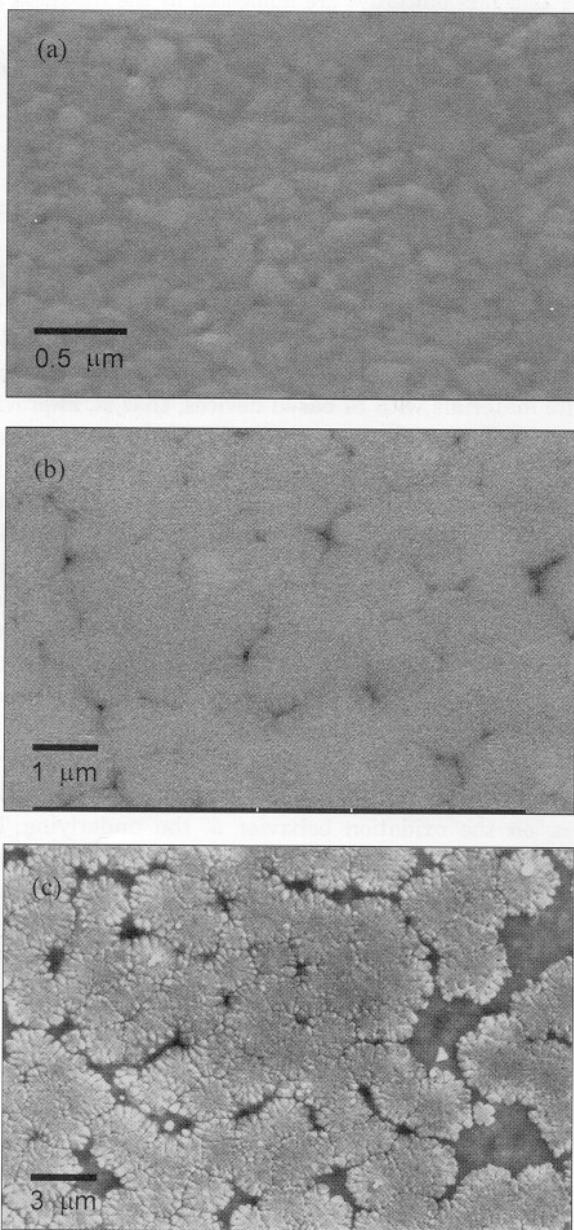


Fig. 3 FESEM micrographs of the PZT film surfaces having IrO₂ bottom-layers with the thickness of (a) 0nm, (b) 10nm and (c) 30nm, respectively.

PZT film on Pt consists of a fine grained structure. In contrast, films on 30nm IrO₂/Pt have a roset structure implying existence of perovskite islands in a pyrochlore matrix. Fig. 4(a) and (b) J-V curves of PZT thin films as a function of IrO₂ thickness in the bottom and top hybrid electrode, respectively. PZT thin films on Pt and 6nm IrO₂/Pt hybrid electrode show excellent leakage current density, which is in the order of 10⁻⁷-10⁻⁸ A/cm² up to 10V, while the films on thicker IrO₂ (15nm and

30nm) bottom hybrid electrode reveal higher leakage current density(10⁻⁶-10⁻⁶ A/cm²). The trend of leakage current density of the PZT films as a function of IrO₂ top hybrid electrode thickness is nearly same when applying same bias conditions as shown in Fig. 4(b).

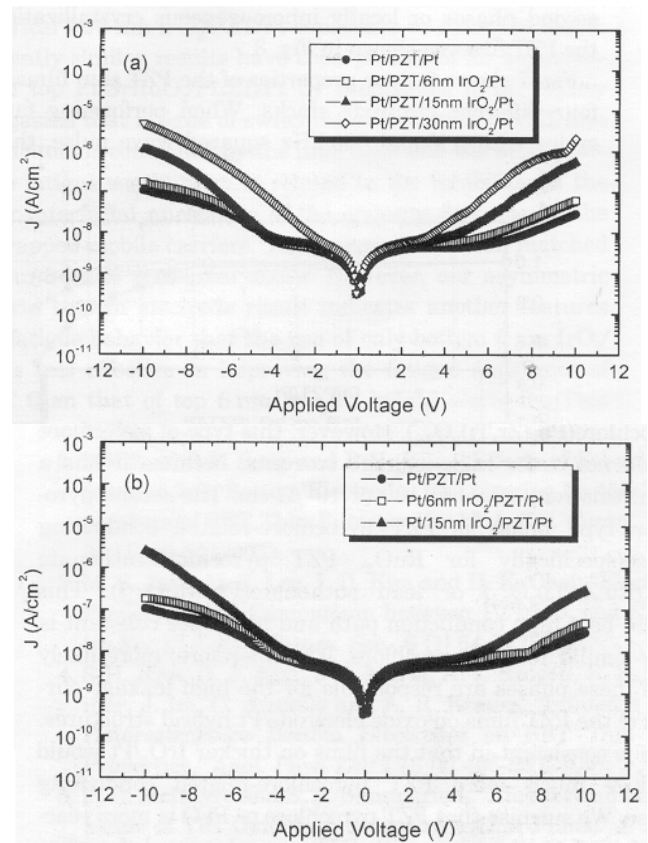


Fig. 4 J-V curves of PZT thin films as a function of (a) bottom IrO₂ and (b) top IrO₂ hybrid electrode thickness.

In general, PZT on oxide electrode has two known pyrochlore-type second phases.^{8,9)} The first is insulating PZT pyrochlore(Pb₂(Zr,Ti)₂O_{7-x}). However, this type of pyrochlore would not cause high leakage currents, because it has a high resistivity of about 10¹⁰ ~ 10¹¹ Ω/cm. The second pyrochlore-type phase is PZT pyrochlore-related conducting phase(specifically for RuO₂, PZT pyrochlore-ruthenate (Pb₂(Ru,Zr,Ti)₂O_{7-x}) or lead ruthenate(Pb₂Ru₂O_{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 IrO₂/Pt would produce much more PZT pyrochlore-related conducting

phase. We surmise that PZT pyrochlore or PbO is more reactive with IrO₂ than it is with PZT perovskite and therefore forms conducting phase very easily like the case of RuO₂. Based on above results and hypothesis, we decide that the optimum thickness of IrO₂ hybrid top and/or bottom electrode is below 10nm(specifically, 6nm in this paper).

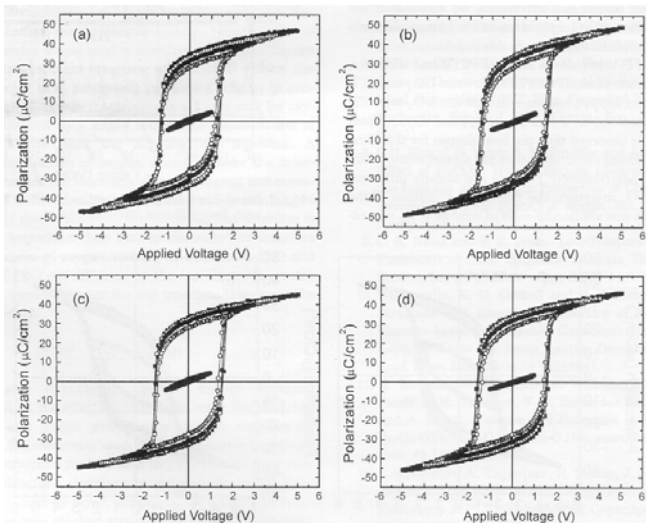


Fig. 5 P-V hysteresis loops of PZT films with four different electrode stacks (a) Pt/PZT/Pt, (b) Pt top/6nm IrO₂/PZT/Pt, (c) Pt/PZT/6nm IrO₂/Pt bottom and (d) Pt top/6nm IrO₂/PZT/6nm IrO₂/Pt bottom as a function of maximum applied voltage from 1V to 5V.

Fig. 5 shows P-V hysteresis loops of PZT films with four different electrode stacks(Pt/PZT/Pt, Pt/6nm IrO₂ top/PZT/Pt, Pt/PZT/6nm IrO₂/Pt bottom and Pt/6nm IrO₂ top/PZT/6nm IrO₂/Pt bottom) as a function of applied voltage from 1V to 5V. It is observed that the loop shapes for the films on the four different electrode stacks are almost same, while the remanent polarization(Pr) values are slightly different. Up to 6nm IrO₂ insertion, the measured Pr values of the PZT thin films are similar(35~38μC/cm² at 5V), regardless of electrode structures. However, the PZT thin films grown on thick IrO₂/Pt hybrid bottom electrode reveal much smaller Pr value(20~25 μC/cm² at 5V) as compared to the films with Pt or 6nm IrO₂/Pt electrode as shown in Fig. 6. The data presented above are entirely consistent with the fact that the Pr 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

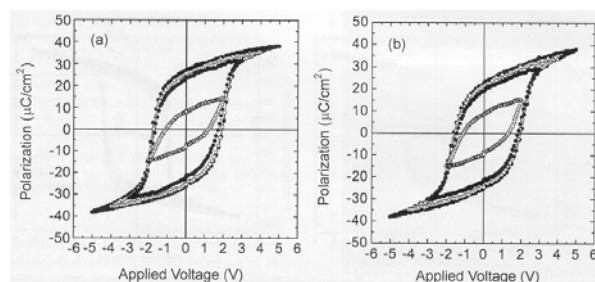


Fig. 6 P-V hysteresis loops of PZT thin films with (a) Pt/PZT/15nm IrO₂/Pt bottom, (b) Pt/PZT/30nm IrO₂/Pt bottom as a function of maximum applied voltage from 2V to 5V.

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 5V and 500kHz squared wave pulse, the Pt/PZT/Pt capacitors show an abrupt polarization decrease between 10⁷ and 10⁹ cycles as expected, whereas PZT with both top and bottom 6nm IrO₂/Pt hybrid electrodes exhibit an almost flat fatigue profile up to 10⁹ 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 RuO₂, IrO₂, SrRuO₃ or hybrid electrodes, incorporated only in both top and bottom electrodes.^{10,11} However, our results indicate that

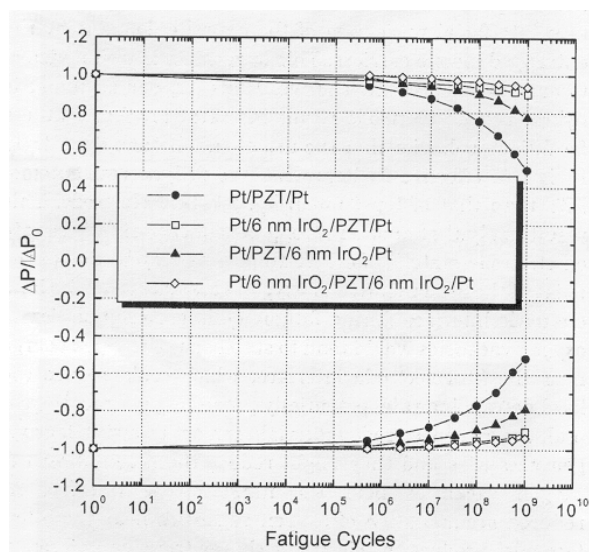


Fig. 7 Normalized fatigue properties of the PZT thin films with four different electrode stacks.

high polarization endurance behavior with fatigue cycles can be obtained even on asymmetrical Pt/6nm IrO₂/PZT/Pt capacitors as shown in Fig.7. Recently similar results have been presented for asymmetrical top Pt/SrRuO₃/PLZT/Pt by Stolichnov 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 6nm IrO₂/Pt is less effective in improving the fatigue resistance of PZT than that of top 6nm IrO₂/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 simply stacked structure of Pt/TiN/poly-Si plug. The right combination of Pt-IrO₂ hybrid electrode showed drastically improved fatigue and other ferroelectric properties of the PZT capacitors.

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