Ferroelectric Nonvolatile Memory Materials: Fundamentals of Reliable Ferroelectric Switching

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Abstract:

Fatigue, defined as loss of polarization under electrical field cycling, is a major obstacle in implementing ferroelectric films into Ferroelectric Random Access Memory (FeRAM/FRAM) non-volatile memories. Little is known about what causes polarization fatigue. It has been suggested that fatigue is related to trapping of carriers injected into $Pb(Zr,Ti)O_3$ (PZT) films from the PZT/electrode interface. It has been proposed that these traps can be optically excited, then measured electrically. This would ultimately lead to a spectroscopy methodology to characterize the trap concentration and energy of the traps. The success of this project depends on creating a thin top electrode such that it does not absorb most of the injected photons, yet still does not affect the electrical measurement.

In this study, various electrode configurations, electrode thicknesses and different electrode materials were examined, and process parameters for optically transparent electrodes were created.

Introduction:

Ferroelectric films such as PZT, have attracted attention for their unique bistable nature, which makes them a candidate for non-volatile capacitor based memories. Polarization fatigue, however, impedes the commercial production of ferroelectric memories. Although the mechanism for fatigue is not known, some models suggest space charge defects accumulating from the ferroelectric/electrode interface as a primary cause.

To characterize the quantity and energy level of these trapped charge defects, optical methods have been suggested. A precise optical device setup will project monochromatic light, ranging from the infrared to the visible, through the top electrode onto the ferroelectric capacitor and excite the trapped charges to the conduction band of PZT. Then an applied voltage bias between the top and bottom electrode allows the charges to be collected thereby characterizing the quantity and energy levels of these charged defects.

In order to realize this characterization, an optically translucent yet continuous top electrode is required. These must behave as good distributors of electric field but also allow light to pass through. The Beer-Lambert Law was used to approximate the absorption of monochromatic light (l=1000 nm) for Pt and Ir electrodes as a function of thickness. For greater than 75% absorption, a thickness of less than 20 nm is needed.

Experimental Procedure and Results:

Translucent top electrodes were created using photolithography and shadow-mask methods. The bottom electrode was Ir. Two different types of top electrode structures were created: a circular structure (Figure 1) and a rib (Figure 2). The rib structure was a non-continuous electrode designed to allow light through yet still distribute a uniform electric field. This allows the rib electrode to be thicker than a continuous electrode. A conventional uniform round electrode was also investigated.

The rib electrode structure was fabricated using standard photolithography using single-layer metal lift-off, whereas the circular design was created using a shadow mask. The rib electrodes were created with Ir and Pt with thicknesses 70 nm and 50 nm, and 50 nm and 20 nm respectively. Circular Ir and Pt electrodes were deposited at thicknesses of 50 nm and 20 nm, and 20 nm and 10 nm, respectively. The thicknesses were measured with a quartz crystal deposition rate monitor.

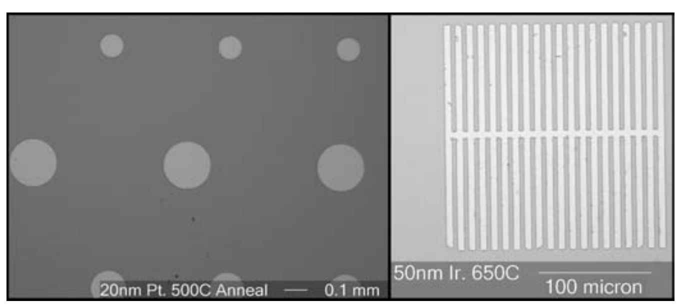

Figure 1, left: 20 nm thick Pt electrodes showing no signs of delamination or defects post-anneal.

Figure 2, right: 50 nm thick optically translucent Ir rib top electrode.

All Pt electrodes appeared uniform after deposition, whereas Ir electrodes showed varied results. Ir rib electrodes of thicknesses 20 nm and 50 nm appeared ragged at the edges, and of lower quality than Pt rib electrodes, but still were a functioning electrode. Ir circular electrodes with thicknesses greater than 20 nm appeared cracked, and pealed (Figure 3) following deposition, while 20 nm thick Ir electrodes appeared visually intact. Visually intact electrodes were annealed with flowing N_2 at 650°C. No delamination was found on the annealed electrodes.

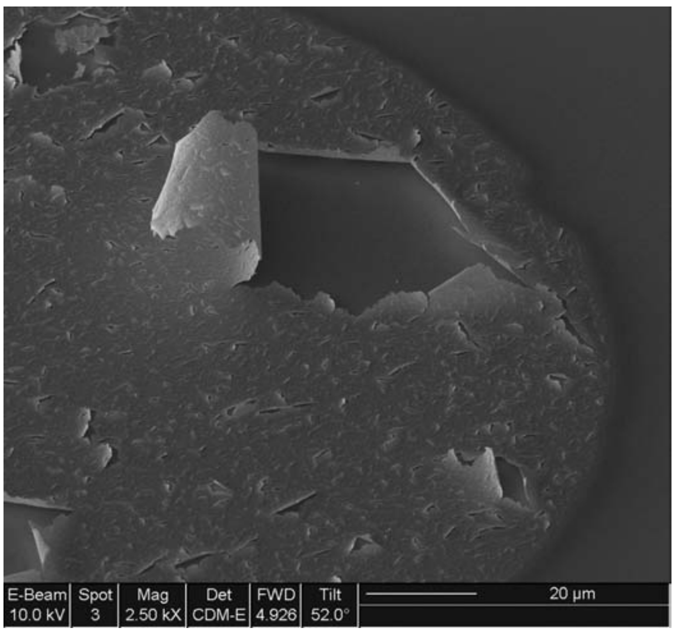

Figure 3: 50 nm thick Ir circular top electrode peeling pre-anneal.

Fatigue properties were characterized by comparing polarization vs. applied electric field (P-E) hysteresis loops at increasing levels of fatigue (0 to 10^7 cycles). Non-annealed Pt and Ir capacitors exhibited greater than 50% relative loss in switchable polarization after 10^4 cycles. Ir electrodes generally exhibited a very small relative change in switchable polarization after 10^7 cycles, whereas some Pt electrodes showed as much as 40% change. Films with Pt top electrodes exhibited higher negative coercive field, while the films with Ir top electrodes exhibited higher positive coercive field (Figure 4).

X-ray photoemission spectroscopy (XPS) was used to characterize the effects of the photolithography and cleaning processes on the chemistry of PZT. This was done at incident angles of 30° and 90°. Two samples were compared, a virgin 90 nm thick PZT film as well as a cleaned (acetone, isopropyl alcohol) and photolithography-processed film. The relative abundance of Pb, Zr, and Ti remained the same for both samples while the relative abundance at 30° of C decreased by 10% and 5% at 90°.

	Type/Thick.	Visual Inspection		Hysteresis		
Pt		Pre-Anneal	Post-Anneal	E_c (V/cm)	- E_c (V/cm)	Rel. Loss in P_{sw}
	Circular					
	10nm	OK	OK	90.7	-101.3	42.5%
	20nm	OK	OK	77.3	-94.7	0.2%
	Rib					
	20nm	OK	OK	66.7	-82.7	59.0%
Ir		Pre-Anneal	Post-Anneal	E_c	- E_c	Rel. Loss in P_{sw}
	Circular					
	20nm	OK	OK	107.8	-93.3	2.0%
	50nm	Peeling	n/a	n/a	n/a	n/a
	70nm	Peeling	n/a	n/a	n/a	n/a
	Rib					
	20nm	OK	OK	64.0	-88.0	2.7%
	50nm	roughness	roughness	72.0	-82.7	2.6%

Figure 4: Physical characteristics of Pt and Ir electrodes of various thicknesses. Coercive field (Ec) and relative loss in switchable polarization after fatigue of 107 cycles.

Conclusions:

Translucent thin Ir and Pt electrodes (10-70 nm) were created on PZT film. Ir electrodes exhibited poor adhesion at thicknesses greater than 20 nm. Pt electrodes adhered well for 10-50 nm of thickness. Annealing at temperatures up to 650°C did not cause defects visible by optical microscope (pre/post anneal comparison). Polarization and leakage current (I-V) measurements were attained for these electrodes, demonstrating that thin non-conventional electrodes can be used for the purpose of the optical spectroscopy method of characterizing charge defects in ferroelectric films.

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References:

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