PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶:
H01L 29/00, 29/40, 29/49, 29/51, H01G
4/005, 4/008, 4/018, 4/33

(11) International Publication Number:

WO 96/21249

(43) International Publication Date:

11 July 1996 (11.07.96)

(21) International Application Number:

PCT/US95/16853

A1

(22) International Filing Date:

22 December 1995 (22.12.95)

(30) Priority Data:

08/365,781

29 December 1994 (29.12.94) US

(60) Parent Application or Grant

(63) Related by Continuation US

08/365,781 (CON)

Filed on

29 December 1994 (29.12.94)

(71) Applicant (for all designated States except US): NORTH CAROLINA STATE UNIVERSITY [US/US]; 103 Holladay Hall, Campus Box 7003, Raleigh, NC 27695-7003 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): KINGON, Angus, I. [ZA/US]; 138 Trafalgar Lane, Cary, NC 27511 (US). ALSHAREEF, Husam, N. [US/US]; Apartment 836, 10700 Academy Road, N.E., Albuquerque, NM 87111 (US). AUCIELLO, Orlando, H. [US/US]; 1008 Medlin Drive, Cary, NC 27511 (US). GIFFORD, Ken, D. [US/US]; 6025 Jordan Woods Drive, Raleigh, NC 27603 (US). LICHTENWALNER, Dan, J. [US/US]; 226 Hillsborough

Street, Raleigh, NC 27603 (US). DAT, Rovindra [US/US]; Apartment 2506, 101 S. Brookside Drive, Dallas, TX 75214 (US).

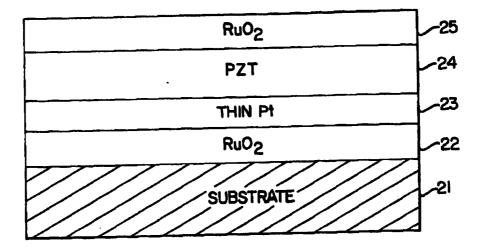
(74) Agents: SIBLEY, Kenneth, D. et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).

(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: HYBRID METAL/METAL OXIDE ELECTRODES FOR FERROELECTRIC CAPACITORS



(57) Abstract

Ferroelectric capacitors with hybrid electrodes including both a conducting oxide (22) and a noble metal (23) may be used to achieve devices having improved performance over capacitors with either platinum or ruthenium oxide electrodes. These hybrid electrode structures can improve capacitor performance both in terms of fatigue and leakage current. Accordingly, these ferroelectric capacitors with hybrid electrodes can be used as elements of an integrated circuit such as a non-volatile memory or dynamic random access memory.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic	SD	Sudan
CF	Central African Republic		of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	Prance	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

5

HYBRID METAL/METAL OXIDE ELECTRODES FOR FERROELECTRIC CAPACITORS

This invention was made with Government support under contract No. N00014-93-1-0591 from the Advanced Research Projects Agency. The Government has certain rights to this invention.

Field of the Invention

This invention relates to capacitors and more particularly to capacitors having hybrid electrode structures.

Background of the Invention

Lead zirconate titanate, Pb(Zr_xTi_{1-x})O₃ or PZT, 10 ferroelectric thin film capacitors have been studied over the past few years as candidates for use in nonvolatile memories. The PZT capacitors are normally fabricated using either metal or oxide electrodes. The most commonly used metal electrode has been Pt, while the most commonly used oxide electrodes have been ruthenium oxide (RuO₂) and lanthanum strontium cobalt oxide (La_{1-x}Sr_xCoO₃). See, R. Ramesh et al., (1992), J. Electronic Materials, Vol. 23, p. 19, (1994); S. Bernstein et al., (1992), J.Mater.Res. 8,12; K. Bellur et al., (1992), Proceedings 20 of the Eighth International Symposium on Applications of Ferroelectrics, IEEE publication No. 92CH3080-9, pp 448; D. Vijay et al., (1992), Proceedings of the Eighth Symposium of Applications International Ferroelectrics, IEEE publication No. 92CH3080-9, 408; R. Dat et al., (1994), Appl. Phys. Lett. 64, 2673; C. Eom et al., (1993), Appl. Phys. Lett. 63, 2570; and O. Auciello et al., (1994), Appl. Phys. Lett. 64, 2873.

However, in both cases the PZT capacitors may have drawbacks which can hamper their use in nonvolatile memories. For example, while Pt/PZT/Pt capacitors have

relatively low leakage current and relatively good dielectric breakdown properties, they may undergo severe polarization fatigue upon repeated switching. On the other hand, oxide/PZT/oxide heterostructures may have excellent resistance to polarization fatigue, but they usually have relatively high leakage currents as compared to Pt/PZT/Pt capacitors and may be more susceptible to dielectric breakdown.

Researchers have attempted to improve the 10 fatigue characteristics of Pt/PZT/Pt capacitors using various approaches. These attempts included donor doping of the $Pb(Zr_xTi_{1-x})O_3$ films as discussed in H. Watanabe et al., (1992), Proceedings of the Fourth International Symposium on Integrated Ferroelectrics pp 346, and J. (1992), Proceedings al., Chen 15 et Symposium onApplications International Ferroelectrics, IEEE No. 92CH3080-9, 111. These attempts also included changing the Zr/Ti ratio as discussed in H. Al-Shareef et al., (1994), Thin Solid Films, 252, 38 (1994), and G. Teowee et al., (1993), MRS Symp. Proc. 310, 20 Still other attempts included the growth of epitaxial PZT thin films as discussed in K. Bellur et al., (1992), Proceedings of the Eighth International Symposium on Applications of Ferroelectrics, publication No. 92CH3080-9, pp 448. Unfortunately, only 25 marginal improvement in the polarization fatigue of Pt/PZT/Pt capacitors could be achieved.

There have also been attempts to reduce the leakage current of PZT films grown on oxide electrodes.

30 In the case of RuO₂, these attempts included annealing the bottom RuO₂ electrode prior to PZT film deposition. H. Al-Shareef et al., Thin Solid Films, 256, 73 (1995). These methods have resulted in some improvement of the leakage characteristics of oxide/PZT/oxide capacitors.

Summary of the Invention

An alternative approach is the use of hybrid (Pt,RuO₂) electrodes. Use of these hybrid electrodes results in PZT thin film capacitors which combine the excellent fatigue characteristics of RuO₂/PZT/RuO₂ capacitors with the relatively low leakage current characteristics of Pt/PZT/Pt capacitors. The presence of RuO2 in the hybrid electrode improves the resistance of PZT capacitors to polarization fatigue. On the other hand, the presence of Pt in the hybrid electrodes lowers the leakage currents of PZT capacitors grown on hybrid (Pt,RuO₂) electrodes. Herein, several types of hybrid electrodes are used to control the electrical properties of PZT thin film capacitors.

In one embodiment of the present invention, a ferroelectric capacitor comprises a first layer of a conducting metal oxide, and a second layer of a metal on the first layer. This capacitor also comprises a third layer of a ferroelectric material on the second layer, and a fourth layer of a conductive material on the third layer.

The conductive metal oxide is preferably ruthenium oxide, iridium oxide, lanthanum strontium cobalt oxide ("LSCO"), indium tin oxide, or yttrium barium copper oxide ("YBCO"), and the second layer is preferably in the range of 50 to 300 Angstroms thick. The metal is preferably a noble metal and most preferable The conductive material preferably comprises platinum. The ferroelectric material may a conductive oxide. include lead zirconate titanate, and the capacitor may be included in an integrated circuit. The capacitor may also comprise a substrate on the first layer opposite the second layer, and this substrate may comprise one of a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, or a silicon dioxide layer on a silicon layer.

30

35

second embodiment of the present invention, the ferroelectric capacitor comprises a first layer of a metal, and a second layer on the first layer. This second layer is a conductive metal oxide and is in 5 the range of 150 to 200 Angstroms thick. embodiment, the capacitor also comprises a third layer of a ferroelectric material on the second layer, and a fourth layer of a conductive material on the third layer.

The conductive metal oxide is preferably 10 ruthenium oxide, iridium oxide, LSCO, indium tin oxide, or YBCO, and the metal is preferably a noble metal and most preferably platinum. The conductive material conductive oxide. The preferably comprises a include lead zirconate ferroelectric material may 15 titanate, and the capacitor may be included in an integrated circuit. In addition, the capacitor may comprise a substrate on the first layer opposite the second layer, and the substrate may comprise one of a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, or a silicon dioxide layer on a silicon layer.

20

30

In a third embodiment of the present invention, ferroelectric capacitor comprises a first including a mixture of a conductive metal oxide and a This capacitor also comprises a second noble metal. layer of a ferroelectric material on the first layer, and a third layer of a conductive material on the second layer.

conductive metal oxide is preferably ruthenium oxide, iridium oxide, LSCO, indium tin oxide, or YBCO. The noble metal is preferably platinum, and the second layer most preferably includes less than about 50 The conductive material atomic percent platinum. conductive The oxide. comprises a preferably material may include lead ferroelectric titanate, and the capacitor may be part of an integrated circuit. The capacitor may also comprise a substrate on the first layer opposite the second layer, and the substrate may comprise one of a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, or a silicon dioxide layer on a silicon layer.

fourth embodiment of the In а invention, a ferroelectric capacitor comprises a first layer including a plurality of alternating interlayers. At least one of the alternating interlayers includes a 10 first metal, and another of the interlayers includes a second metal or a conducting oxide. The capacitor also comprises a second layer of a ferroelectric material on the first layer, and a third layer of a conductive material on the second layer. 15

The first metal is preferably a noble metal, and is most preferably platinum. At least one of the alternating interlayers may include a noble metal, and the interlayers may include ruthenium, another of iridium, ruthenium oxide, iridium oxide, 20 strontium cobalt oxide, indium tin oxide, or YBCO. conductive material preferably comprises a conductive The ferroelectric material may include lead oxide. zirconate titanate, and the capacitor may be included in an integrated circuit. The capacitor may also comprise 25 a substrate on the first layer opposite the second layer, and the substrate may comprise a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, or a silicon dioxide layer on a silicon layer. In addition, the capacitor may include a primary layer of a primary metal on the first layer opposite the second layer, and this primary metal may comprise a noble metal such as platinum.

In a fifth embodiment of the present invention, a ferroelectric capacitor comprises a first layer of a metal, and a second layer of a conductive metal oxide on

the first layer. This capacitor also comprises a third layer of a ferroelectric material on the second layer, and a fourth layer of the conductive metal oxide on and in direct contact with the third layer.

5 The conductive metal oxide is preferably ruthenium oxide, iridium oxide, LSCO, indium tin oxide, or YBCO, and the metal is preferably a noble metal, most preferably platinum. The ferroelectric material may include lead zirconate titanate, and the capacitor may be 10 part of an integrated circuit. The capacitor may also comprise a substrate on the first layer opposite the second layer, and the substrate may comprise one of a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, and a silicon dioxide layer on a 15 silicon layer.

Brief Description of the Drawings

Figure 1(a) illustrates a cross-sectional view of a PZT capacitor with a thin Pt/RuO_2 hybrid bottom 20 electrode.

Figure 1(b) illustrates a cross-sectional view of a PZT capacitor with a thin ${\rm RuO_2/Pt}$ hybrid bottom electrode.

Figure 1(c) illustrates a cross-sectional view 25 of a PZT capacitor with a co-deposited Pt-RuO₂ hybrid bottom electrode.

Figure 2 shows fatigue curves of Pt/PZT/Pt/MgO (indicated by squares with a diagonal slash) and $RuO_2/PZT/RuO_2/MgO$ (indicated by filled diamonds) capacitors. The fatigue tests were performed at 500 kHz. The vertical axis denotes values of (P^*-P^*) in units of $\mu C/cm^2$, and the horizontal axis denotes cycles. The Pt/PZT/Pt/MgO data was obtained with a 5 volt signal, and the $RuO_2/PZT/RuO_2/MgO$ data was obtained with a 3 volt signal.

35

Figure 3 shows the time dependence of the DC electrical current of Pt/PZT/Pt/MgO (indicated by squares with a diagonal slash) and RuO₂/PZT/RuO₂/MgO (indicated by filled diamonds) capacitors. The vertical axis denotes values of current in units of A/cm², and the horizontal axis denotes time in units of seconds. The data was obtained with a 1 volt signal and a $100X100\,\mu\text{m}^2$ contact.

Figure 4 shows I-t curves for: $RuO_2/PZT/RuO_2$ capacitor (indicated by filled diamonds); (b) an RuO₂/PZT/(Pt-RuO₂) capacitor (indicated by circles 10 with a dot); (c) an RuO₂/PZT/100APt/RuO₂ (Pt grown at RT) capacitor (indicated by unfilled triangles); (d) RuO₂/PZT/200ARuO₂/Pt/RuO₂ capacitor (indicated by unfilled circles); (e) an RuO₂/PZT/100APt/RuO₂ (Pt grown at 400°C) capacitor (indicated by squares with a dot); and (f) a 15 Pt/PZT/Pt capacitor (indicated by squares with a diagonal slash). The vertical axis denotes values of current in units of A/cm2, and the horizontal axis denotes time in units of seconds. The data was obtained with a 1 volt signal, and each sample was provided on a MgO substrate 20 with a (100) orientation.

Figure 5 shows fatigue curves for: (a) RuO₂/PZT/RuO₂ capacitor (indicated by filled diamonds); (b) an $RuO_2/PZT/(Pt-RuO_2)/RuO_2$ capacitor (indicated by filled circles); (c) an $RuO_2/PZT/100\mbox{\normalfont\AAPt/RuO}_2$ (Pt grown at 25 RT) capacitor (indicated by unfilled triangles); (d) an RuO₂/PZT/100APt/RuO₂ (Pt grown at 400°C) capacitor (e) squares with а dot); by (indicated $RuO_2/PZT/200\mbox{\normalfont\AA}RuO_2/Pt/RuO_2$ capacitor (indicated by unfilled circles); and (f) a Pt/PZT/Pt capacitor (indicated by squares with a diagonal slash). The vertical axis denotes values of (P*-P*) in units of μ C/cm², and the horizontal axis denotes cycles. The data was obtained with a 3-5 volt 500 kHz signal, and each sample was provided on a MgO substrate with a (100) orientation.

-8-

Figure 6 illustrates a cross-sectional view of a PZT capacitor with alternating bottom layers of Pt and RuO2 or alternating bottom layers of Pt and Ru.

Figure 7(a) shows a hysteresis loop for a 5 RuO₂/PZT/100ÅPt/RuO₂/SiO₂/Si capacitor. The vertical axis denotes values of polarization in units of $\mu C/cm^2$, and the horizontal axis denotes values of the electric field in units of kV/cm. The data was obtained with a 4 volt signal and a $100X100\mu m^2$ contact.

Figure 7(b) shows a fatigue curve for a RuO₂/PZT/100ÅPt/RuO₂/SiO₂/Si capacitor. The vertical axis denotes values of (P^*-P^*) in units of $\mu C/cm^2$, and the horizontal axis denotes cycles. The data was obtained with a 4 volt 500 kHz signal.

10

25

35

Figure 7(c) shows a time dependence of the DC 15 current of a RuO₂/PZT/100ÅPt/RuO₂/SiO₂/Si electrical The vertical axis denotes values of current capacitor. in units of A/cm², and the horizontal axis denotes time in units of seconds. The data was obtained with an input 20 voltage of 1 volt and a contact area of 100X100μm²

Detailed Description of the Invention

The present invention will now be described more fully hereinafter with reference to the accompanying in which a preferred embodiment of drawings, invention is shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiment set forth herein; rather, this embodiment is provided so that disclosure will be thorough and complete, and will fully 30 convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout.

Referring now to Figure 1(a), there is shown a first embodiment of a ferroelectric capacitor with a RuO₂/PZT/Pt/RuO₂ capacitor structure according to the The capacitor is formed on a present invention. substrate 21 which may comprise either a magnesium oxide

layer, or a silicon substrate layer with a silicon dioxide layer adjacent the capacitor structure. substrate may alternately comprise a silicon layer, a gallium arsenide layer, a silicon carbide layer, sapphire layer, or layers of other materials known to those having skill in the art. The bottom electrode of the capacitor has a first conducting oxide (preferably RuO₂) layer 22 on the substrate, and a second metal (preferably a noble metal) layer 23 on the conducting of 24 a ferroelectric material A layer oxide. 10 (preferably PZT) is provided on the metal layer 23, and a conducting layer (preferably a conducting oxide) 25 is provided on the ferroelectric material to form a top electrode.

The metal layer 23 is preferably a thin Pt 15 layer on the order of 50Å to 300Å thick. A thin Pt layer significantly degrade the ferroelectric properties of the capacitor, while thicker Pt layers may result in polarization fatigue. In addition, the thin Pt layer improves the leakage current behavior of the 20 capacitor increasing its utility in non-volatile memory It is believed that the thin Pt layer applications. controls nucleation of the perovskite phase PZT and minimizes the formation of a deleterious pyrochlore The thin Pt layer also reduces property phase. 25 variability of the PZT film from device to device on the same substrate as well as from substrate to substrate and batch to batch.

Referring now to Figure 1(b), there is shown a second embodiment of a ferroelectric capacitor with an RuO₂/PZT/RuO₂/Pt structure according to the present invention. The capacitor is formed on a substrate 21' which may comprise either a magnesium oxide layer, or a silicon substrate layer with a silicon dioxide layer adjacent the capacitor structure. The substrate may alternately comprise a silicon layer, a gallium arsenide layer, a silicon carbide layer, a sapphire layer, or

layers of other materials known to those having skill in The bottom electrode of the capacitor has a first metal (preferably a noble metal) layer 26 on the substrate, and a conducting oxide (preferably RuO2) layer 27 on the metal layer. A layer 24' of a ferroelectric material (preferably PZT) is provided on the conducting oxide layer 27, and a conducting layer (preferably a conducting oxide) 25' is provided on the ferroelectric material to form a top electrode. The conducting oxide layer 27 preferably comprises an RuO2 layer having a 10 thickness on the order of 150-200Å. This RuO, layer polarization leakage without compromising improves current leakage.

Referring now to Figure 1(c), there is shown a third embodiment of a ferroelectric capacitor with an 15 RuO₂/PZT/(Pt-RuO₂) structure according to the present The capacitor is formed on a substrate 21" which may comprise either a magnesium oxide layer, or a silicon substrate layer with a silicon dioxide layer adjacent the capacitor structure. The substrate may alternately comprise a silicon layer, a gallium arsenide layer, a silicon carbide layer, a sapphire layer, or layers of other materials known to those having skill in The bottom electrode of the capacitor is a the art. layer 28 of a co-deposited noble metal (preferably Pt) 25 and a conducting oxide (preferably RuO2). A layer 24" of a ferroelectric material (preferably PZT) is provided on the cod-deposited layer 28, and a conducting layer (preferably a conducting oxide) 25" is provided on the ferroelectric material to form a top electrode. 30

In each of the embodiments illustrated in Figures 1(a-c), the noble metal may comprise one of platinum, palladium, or gold, with platinum being preferred. The conducting oxide may comprise one of iridium oxide, ruthenium oxide, lanthanum strontium cobalt oxide ("LSCO"), indium tin oxide, or yttrium barium copper oxide ("YBCO"), with ruthenium oxide being

35

preferred. The ferroelectric material is preferably a mixture or solution of lead, zirconium, and titanium which forms a perovskite structure and is known as PZT. PZT variants may also be used and these variants may include a dopant or substitution such as lanthanum, tin, or niobium as will be understood by one having skill in the art. In addition, other ferroelectric materials which show fatigue on metal electrodes may be used.

Each of these layers of metals, metal oxides, 10 and ferroelectric materials may be deposited by methods ion cluster beam deposition, such as sputtering, evaporation, molecular beam epitaxy, ion plating, magnetron sputter deposition, ion beam sputter deposition, sol-gel deposition, laser ablation deposition, or other methods known to those having skill 15 in the art. Various deposition techniques are discussed, for example, in U.S. Patent No. 5,142,437 entitled "Conducting Electrode Layers For Ferroelectric Capacitors In Integrated Circuits And Method" to Kammerdiner et al., and U.S. Patent No. 5,270,298 entitled "Cubic Metal Oxide 20 Thin Film Epitaxially Grown On Silicon" to Ramesh. Both of the above mentioned patents are hereby incorporated in their entirety herein by reference.

Furthermore, the top electrode in each of Figures 1(a-c) respectively comprises a conductive layer 25 25, 25', and 25". This conductive layer is preferably a layer of a conductive oxide such a ruthenium oxide (RuO2), LSCO, iridium oxide, indium tin oxide, or YBCO (YBa₂Cu₃O₇ ,), but may also include a noble metal such as Pt. Accordingly, the top electrode may comprise a hybrid 30 electrode structure such as those discussed above with regard to the bottom electrodes. For example, the top electrode may comprise a Pt/RuO2 structure, an RuO2/Pt structure, or a co-deposited Pt-RuO2 structure. addition, the top electrode may comprise alternating 35 layers as discussed with regard to the bottom electrode of Figure 6.

Referring now to Figure 2, there are shown fatigue curves for typical Pt/PZT/Pt/MgO and $RuO_2/PZT/RuO_2/MgO$ capacitor structures. The fatigue tests were performed at 500 kHz. The capacitor with RuO_2 electrodes has (P^*-P^*) values that are essentially constant up to $4X10^{10}$ switching cycles. In comparison, the capacitor with Pt electrodes has (P^*-P^*) values that have decayed significantly by $3X10^{10}$ switching cycles.

Referring now to Figure 3, there is shown the time dependence of the DC electrical current for typical Pt/PZT/Pt/MgO and RuO₂/PZT/RuO₂/MgO capacitor structures. While the capacitor with RuO₂ electrodes has superior fatigue characteristics, the capacitor with the Pt electrodes has a much lower leakage current. As shown, the capacitor with RuO₂ electrodes has a leakage current that is several orders of magnitude higher than the capacitor with Pt electrodes.

Referring now to Figure 4, there are shown I-t curves for: (a) an RuO₂/PZT/RuO₂ capacitor; (b) RuO₂/PZT/(Pt-RuO₂) capacitor; (c) an RuO₂/PZT/100APt/RuO₂ grown at RT) capacitor; capacitor (Pt (e) RuO₂/PZT/200ÅRuO₂/Pt/RuO₂ capacitor; an $RuO_2/PZT/100\mbox{\normalfont\AA}Pt/RuO_2$ (Pt grown at 400°C) capacitor; and (f) a Pt/PZT/Pt capacitor. A typical RuO₂/PZT/RuO₂ is indicated as sample (a) and has a leakage current that is roughly two orders of magnitude higher than any of the capacitors with hybrid electrodes which are indicated as samples (b), (c), (d), and (e).

20

25

Referring now to Figure 5, there are shown fatigue curves for: (a) an $RuO_2/PZT/RuO_2$ capacitor; (b) an $RuO_2/PZT/(Pt-RuO_2)/RuO_2$ capacitor; (c) an $RuO_2/PZT/100\text{\AA}Pt/RuO_2$ (Pt grown at RT) capacitor; (d) an $RuO_2/PZT/100\text{\AA}Pt/RuO_2$ (Pt grown at 400°C) capacitor; (e) an $RuO_2/PZT/200\text{Å}RuO_2/Pt/RuO_2$ capacitor; and (f) a Pt/PZT/Pt capacitor. The typical Pt/PZT/Pt capacitor, represented as sample (f), has a magnitude of $(P*-P^*)$ that drops to approximately 5 μ C/cm² after approximately 3X10¹º cycles.

In comparison, each of the capacitors with hybrid electrodes, represented as samples (b), (c), (d), and (e), maintains a (P*-P^) magnitude of approximately 35 μ C/cm² or greater after 3X10¹⁰ cycles.

Referring now to Figure 6, there is shown a 5 fourth embodiment of a ferroelectric capacitor wherein the bottom electrode comprises a plurality of alternating These alternating layers are preferably layers. alternating layers of Pt and RuO2, or alternating layers 10 of Pt and Ru. The capacitor is formed on a substrate 21''' which may be either a magnesium oxide layer, or a silicon substrate layer with a silicon dioxide layer adjacent the capacitor structure. The substrate may alternately comprise a silicon layer, a gallium arsenide layer, a silicon carbide layer, a sapphire layer, layers of other materials known to those having skill in the art. The bottom electrode of the capacitor comprises a structure of alternating layers 30_1 , 31_1 , 30_2 , 31_2 , and Layers 30₁, 30₂, and 30₃ may comprise iridium, 20 ruthenium, iridium oxide, ruthenium oxide, LSCO, indium tin oxide, or YBCO. Layers 31, and 31, may comprise a noble metal such as platinum, gold, or palladium. bottom electrode may also comprise an optional primary layer 29 of a noble metal (preferably Pt). A layer 24''' of a ferroelectric material (preferably PZT) is provided 25 the second layer 30, and a conducting (preferably a conducting oxide) 25''' is provided on the ferroelectric material to form a top electrode.

In a preferred embodiment, layers $30_{(1-3)}$ comprise a conductive oxide (preferably RuO_2) or a metal (preferably Ru), and layers $31_{(1-2)}$ comprise a noble metal (preferably Pt). While five alternating layers are shown, it will be understood that this bottom electrode structure may include any number of alternating layers. Preferably, each layer $30_{(1-m)}$ and $31_{(1-n)}$ is in the range of $10\text{\AA}-300\text{\AA}$ thick, and the total thickness for this structure of alternating layers $30_{(1-m)}$ and $31_{(1-n)}$ is in the

-14-

range of 800Å-3000Å thick. In addition, the first layer may be either a layer 30_1 or 31_1 , and the last layer may be either a layer 30_m or 31_n .

The noble metal may comprise one of platinum, palladium, or gold, with platinum being preferred. The ferroelectric material is preferably a mixture or solution of lead, zirconium, and titanium which forms a perovskite structure and is known as PZT. PZT variants may also be produced and these variants may include a dopant or substitution such as lanthanum, tin, or niobium as will be understood by one having skill in the art. In addition, other ferroelectric materials which show fatigue on metal electrodes may be used.

Each of these layers of metals, conductive oxides, and ferroelectric materials may be deposited by methods such as ion cluster beam deposition, sputtering, evaporation, molecular beam epitaxy, ion plating, sputter deposition, ion beam magnetron sputter deposition, sol-qel deposition, laser ablation, or other methods known to those having skill in the art. deposition techniques are discussed in U.S. Patent No. 5,142,437 entitled "Conducting Electrode Layers Ferroelectric Capacitors In Integrated Circuits Method" to Kammerdiner et al., and U.S. Patent No. "Cubic Metal Oxide Thin 5,270,298 entitled Film Epitaxially Grown On Silicon" to Ramesh. Both of the above mentioned patents are hereby incorporated in their entirety herein by reference.

15

20

25

Furthermore, the top electrode in Figures 6 comprises a conductive layer 25'''. This conductive layer is preferably a layer of a conductive oxide such as ruthenium oxide (RuO₂), iridium oxide, LSCO, indium tin oxide, or YBCO, and this electrode may also include a noble metal such as Pt. Accordingly, the top electrode may comprise a hybrid electrode structure such as those discussed above with regard to the bottom electrodes. For example, the top electrode may comprise a Pt/RuO₂

10

structure, an RuO2/Pt structure, or a co-deposited Pt-RuO, In addition, the top electrode may comprise alternating layers of Ru or RuO2 and Pt.

Each of the capacitors with hybrid electrodes, 5 illustrated in Figures 1(a-c) and 6, is preferably included as an element in an integrated circuit chip such as a non-volatile memory or a dynamic random access Accordingly, a plurality of ferroelectric memory. capacitors with hybrid electrodes can be manufactured simultaneously on a single integrated circuit chip.

Referring now to Figures 7(a-c), there are respectively shown a hysteresis loop, a fatigue curve, and DC electrical current time dependence curve for an $RuO_2/PZT/100\text{ÅPt}/RuO_2/SiO_2/Si$ capacitor structure. 15 capacitor structure maintains a (P*-P^) magnitude of approximately 20 $\mu\text{C/cm}^2$ at $3\text{X}10^{10}$ cycles. This capacitor structure also has a leakage current of approximately $2X10^{-7} \text{ A/cm}^2$ at one second and approximately $2X10^{-9} \text{ A/cm}^2$ at 6X102 seconds.

EXAMPLES 20

Five capacitor types are prepared for this study. Three of the capacitor types had hybrid (Pt, RuO_2) bottom electrodes with the following structures: RuO₂/PZT/RuO₂/Pt/MgO; RuO₂/PZT/Pt/RuO₂/MgO; $RuO_2/PZT/(Pt-RuO_2)/MgO$. Schematic illustrations of each 25 of these capacitor structures are shown respectively in Figures 1(a), 1(b), and 1(c). The other two capacitor types, which are included for comparison, had similar top and bottom electrodes with the following structures: Pt/PZT/Pt/MgO and RuO₂/PZT/RuO₂/MgO. Details of the Pt 30 and RuO_2 deposition conditions are discussed in H. Al-Shareef et al., (1993), Integrated Ferroelectrics 3, 321.

case of the RuO₂/PZT/Pt/RuO₂/MgO the In capacitor, shown in Figure 1(a), a Pt interlayer 22 (on the order of 100Å thick) was deposited on the bottom \mbox{RuO}_2 electrode 21, prior to PZT film 24 growth, both by ion

10

15

20

25

beam sputter-deposition (at 400°C) and by magnetron sputter-deposition (at room temperature). In the case of the RuO₂/PZT/RuO₂/Pt/MgO capacitor, shown in Figure 1(b), an RuO₂ interlayer 27 (on the order of 200Å thick) was deposited by ion beam sputter-deposition at 400°C on the Pt bottom electrode 26 prior to PZT film 24' growth. For the RuO₂/PZT/(Pt-RuO₂)/MgO capacitor, shown in Figure 1(c), the bottom electrode was a co-deposited Pt-RuO₂ layer 28. The Pt-RuO₂ layer 28 was grown using ion beam sputter-deposition at 400-500°C. The sputtering target included both Pt and Ru metals.

PZT thin films 24, 24', and 24'' (0.2-0.25 μm thick) were subsequently deposited on the Pt, RuO2, and the hybrid bottom electrodes using a spin-on sol-gel described in R. Schwartz process al., Matt.Res.Soc.Symp. 243, pp 245. The solution used to make the PZT films for this study had a Zr/Ti ratio of 53/47 and a 5mol% excess Pb to compensate for lead loss during annealing. Each film was formed by multilayer deposition, with each layer initially heat treated at 300°C for 5 minutes in air. The films were finally crystallized by annealing at 700°C for 10 minutes in air. The PZT thin film may also be created by other methods deposition, ion cluster beam sputtering, as evaporation, molecular beam epitaxy, ion plating, sputter deposition, ion beam sputter magnetron deposition, sol-gel deposition, laser ablation, or other methods known to those having skill in the art.

For all capacitors, except the Pt/PZT/Pt/MgO capacitor, RuO₂ top electrodes 25, 25', and 25'' were deposited on the PZT films using ion beam sputter-deposition. The top electrodes were patterned using standard photolithographic techniques and the ion beam etching (500 eV, 8 mA Ar' ion beam). After patterning of the top electrodes, the entire capacitor stack was annealed at 550°C for 10 minutes in air. Alternately, hybrid electrodes, such as Pt/RuO₂ electrodes, RuO₂/Pt

electrodes, co-deposited $Pt-RuO_2$ electrodes, or electrodes with alternating layers of Pt and RuO_2 , may be used as the top electrodes 25, 25', and 25''.

Before the properties of PZT capacitors with 5 hybrid (Pt,RuO2) electrodes are discussed, it is useful to present first the typical electrical characteristics of Pt/PZT/Pt and $RuO_2/PZT/RuO_2$ capacitors. The fatigue and DC leakage characteristics of typical Pt/PZT/Pt/MgO and RuO₂/PZT/RuO₂/MgO capacitors are shown in Figures 2 and 3, Notice that the difference between the respectively. 10 switched and non-switched polarizations $(P*-P^{*})$ decays by nearly 95% after $3x10^{10}$ cycles in the case of the electrodes (the Pt/PZT/Pt/MgO Pt with capacitor capacitors have in some cases shown only 50% drop in (P*-P^), but most samples typically show more than 90% drop). 15 In comparison the $(P*-P^{^{*}})$ value of the $RuO_2/PZT/RuO_2/MgO$ capacitor remains essentially constant up to 4X1010 While the capacitor with switching cycles. electrodes has superior fatigue, it has much higher leakage current than the Pt/PZT/Pt/MgO capacitor as shown 20 in Figure 3. Notice that the $RuO_2/PZT/RuO_2/MgO$ capacitor has a leakage current that is several orders of magnitude higher than the Pt/PZT/Pt/MgO capacitor.

The hybrid (Pt,RuO₂) electrode concept was developed based on the observation that nucleation of 25 single phase perovskite PZT films is easier to achieve on Pt than on RuO_2 electrodes as discussed in Al-Shareef, H.N., Bellur, K.R. Auciello, O., and Kingon, A.I., Ferroelectrics, Vol. 152, p. 85, (1994). PZT films grown on Pt were characterized by a high nucleation site 30 density and were phase-pure perovskite. In comparison, the films grown on RuO_2 were characterized by a low nucleation site density and contained a non-ferroelectric conductive second phase as discussed in Al-Shareef, H.N., Auciello, 0., and Kingon, Bellur, K.R. (1994).Thus, 85, Ferroelectrics, Vol. 152, p. combining Pt and RuO_2 into one bottom electrode (hence the

10

15

20

25

30

35

-18-

term hybrid electrode), one can enhance nucleation and crystallization of perovskite PZT, thereby eliminating the second phase and reducing the leakage current of the capacitors. If the amount of Pt in the hybrid electrode is properly controlled, the excellent resistance to fatigue can also be maintained.

Three hybrid electrode types were evaluated. The first included a thin Pt layer 23 on a bottom RuO₂ electrode 22 as shown in Figure 1(a); the second included a thin RuO, layer 27 on a bottom Pt electrode 26 as shown in Figure 1(b); and the third included a co-deposited (Pt-RuO₂) layer 28 used as a bottom electrode as shown in Figure 1(c). The electrical properties (DC leakage, and fatigue) of PZT capacitors grown by the sol-gel process on these three hybrid electrodes are shown in Figures 4 The fatigue and leakage behavior of Pt/PZT/Pt/MgO and RuO₂/PZT/RuO₂/MgO are also included in Figures 4 and 5 to facilitate comparison. These hybrid electrodes may be used with PZT layers formed by deposition methods such as ion cluster beam deposition, sputtering, evaporation, molecular beam epitaxy, plating, magnetron sputter deposition, ion beam sputter deposition, sol-gel deposition, laser ablation, or other methods known to those having skill in the art.

Two PZT capacitors with RuO₂/PZT/100ÅPt/RuO₂/MgO heterostructures shown in Figure 1(a) were tested. One had a Pt interlayer produced by magnetron sputter-deposition at room temperature, while the other had a Pt interlayer produced by ion beam sputter-deposition at 400°C. Capacitors of this type typically had a remanent polarization of about 35-40 μ C/cm² and they were fully switched at 3-4 Volts. typical hysteresis loops (data not shown), the actual remanent polarization value (+Pr) appears to be smaller than it actually is due to the asymmetry of the loop along the field axis. This asymmetry results because the top and bottom electrodes are different, and the bottom

25

30

35

electrode is usually exposed to higher temperatures (during film deposition) than the top one. Figure 4 shows that the RuO₂/PZT/100APt/RuO₂/MgO sample (c) capacitor (with Pt interlayer deposited by magnetron 5 sputtering at room temperature) has two orders of magnitude lower leakage current than does the typical RuO₂/PZT/RuO₂/MgO capacitor, sample (a). In comparison, (e) also shows that 4 sample Figure RuO₂/PZT/100ÅPt/RuO₂/MgO capacitor (with Pt interlayer 10 deposited by ion beam sputtering at 400°C) has four orders of magnitude lower leakage current than does the $RuO_2/PZT/RuO_2/MgO$ capacitor, sample (a). This reduction in leakage current is achieved without compromising the fatigue behavior usually observed excellent ${\rm RuO_2/PZT/RuO_2}$ capacitors without a Pt interlayer. As can samples (c) and Figure 5 seen in RuO₂/PZT/100APt/RuO₂/MgO capacitors show negligible fatigue up to 3x1010 cycles.

The above data shows that using a thin Pt 20 interlayer (on the order of 100\AA) between the PZT film and the bottom RuO_2 electrode reduces the leakage current of PZT capacitors while maintaining an excellent resistance to polarization fatigue.

The capacitors with the 100Å Pt interlayer deposited at room temperature by magnetron sputtering usually have higher leakage current and better fatigue than the capacitors with the 100Å Pt interlayer deposited by ion beam sputter-deposition at 400°C. The Pt films grown by ion beam sputtering (at 400°C) are more dense than those grown by magnetron sputter-deposition (at room temperature) as discussed in P. Hren et al., (1992), Integrated Ferroelectrics 2, 311. Therefore, more RuO₂ is expected to be in contact with the PZT film in the case of the capacitors with the 100Å Pt interlayer grown at room temperature. That is why the properties of the RuO₂/PZT/100ÅPt/RuO₂/MgO capacitor (with room temperature

-20-

deposited Pt interlayer) are closer to those of RuO₂/PZT/RuO₂/MgO capacitors.

TEM observation has revealed no apparent second PZT films grown on 100APt/RuO2 in phases 5 electrodes. The presence of the Pt interlayer appears to have increased the nucleation site density and enhanced crystallization of single phase perovskite PZT.

The second hybrid electrode type included a thin RuO, layer on a Pt bottom electrode. PZT capacitors this hybrid electrode 10 type an RuO₂/PZT/200ÅRuO₂/Pt/MgO heterostructure as shown in 1(b). This capacitor type has a remanent polarization of about $40\mu\text{C/cm}^2$ and it is well saturated at 40 Volts (data not shown). The leakage current and fatique behavior of this capacitor type are shown in 15 Figures 4 and 5, respectively. Figure 4 sample (d) shows that this capacitor type has a leakage current of about 5X10⁻⁸ A/cm² (at 1 Volt). This is nearly five orders of magnitude lower than the leakage current of a typical RuO₂/PZT/RuO₂/MgO capacitor. The fatigue curve of this 20 capacitor type (RuO₂/PZT/200ÅRuO₂/Pt/MgO) shows about a 50% drop in the magnitude of (P*-P^) after 3X10¹⁰ switching cycles. This is shown in Figure 5 as sample (e). However, it can be seen that the magnitude of (P*- P^{\bullet}) is beginning to level off to a value of 35 μ C/cm₂.

The third hybrid electrode type included a Pt-RuO, co-deposited layer. The co-deposited layer is formed by sputtering a target that includes both Pt and Ru metals. The Pt-RuO, layer was used as a bottom electrode to produce RuO₂/PZT/Pt-RuO₂/MgO capacitors as shown in Figure 1(c).

25

30

35

The electrical properties of such capacitors were dependent on the composition of the Pt-RuO2 codeposited layer. For a Pt-RuO2 layer with 50 atomic %Pt (determined by RBS), the properties are also shown in Figure 4 sample (b) and Figure 5 sample (b).

15

25

30

35

As seen in Figure 4 sample (b), this capacitor has a leakage current that is two orders of magnitude of typical leakage current a the than lower RuO₂/PZT/RuO₂/MgO capacitor indicated as sample (a). 5 Figure 5 sample (b) shows that this capacitor type has good fatigue behavior, where (P*-P^) decays about 20% after $5x10^{10}$ switching cycles. It should be added here that when a $PT-RuO_2$ layer with 80 atomic %Pt was used as a bottom electrode in an $RuO_2/PZT/Rt-RuO_2/MgO$ capacitor, the value of (P*-P^) dropped by 70% after 5x10¹⁰ cycles; the leakage current of such a capacitor was less than 10-9 A/cm² (at 1 Volt) (data not shown).

The results discussed above show that there is a trade-off between the resistance to polarization fatigue and the resistivity or leakage current level of Therefore, one has to manipulate the PZT capacitors. thicknesses of the Pt and RuO2 interlayers (in the case of the Pt/RuO_2 and RuO_2/Pt hybrid electrodes) and the $Pt-RuO_2$ composition (in the case of the co-deposited hybrid electrodes) to achieve the optimum leakage current and 20 fatigue of PZT capacitors.

Three types of (Pt,RuO2) hybrid electrodes were evaluated as replacements for the bottom RuO_2 electrode in RuO₂/PZT/RuO₂ capacitors. Each hybrid electrode type was evaluated in terms of its effect on the leakage current, PZT retention loss of and fatique, polarization capacitors as compared to $RuO_2/PZT/RuO_2$ capacitors. It was shown that using hybrid electrodes can result in PZT capacitors with leakage currents two to four orders of magnitude lower than those of a typical $RuO_2/PZT/RuO_2$ capacitor. This reduction in leakage current is achieved while at the same time maintaining the excellent resistance to polarization fatigue characteristic of the ${\rm RuO_2/PZT/RuO_2}$ capacitors. In addition, it was shown that all capacitors with hybrid electrodes have negligible retention loss.

-22-

The foregoing examples are illustrative of the present invention, and are not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

THAT WHICH IS CLAIMED IS:

- 1. A ferroelectric capacitor comprising:
- a first layer comprising a conducting metal oxide;
- a second layer on said first layer, said second layer comprising a metal;
 - a third layer on said second layer opposite said first layer, said third layer comprising a ferroelectric material; and
- a fourth layer on said third layer opposite 10 said second layer, said fourth layer comprising a conductive material.
- A ferroelectric capacitor according to Claim 1 wherein said conductive metal oxide comprises one of ruthenium oxide, iridium oxide, lanthanum strontium
 cobalt oxide, indium tin oxide, or yttrium barium copper oxide.
 - 3. A ferroelectric capacitor according to Claim 1 wherein said second layer is in the range of 50 to 300 Angstroms thick.
- 20 4. A ferroelectric capacitor according to Claim 1 wherein said metal comprises a noble metal.
 - 5. A ferroelectric capacitor according to Claim 4 wherein said noble metal comprises platinum.
- 6. A ferroelectric capacitor according to 25 Claim 1 wherein said conductive material comprises a conductive oxide.
 - 7. A ferroelectric capacitor according to Claim 1 wherein said ferroelectric material comprises lead zirconate titanate.

-24-

- 8. A ferroelectric capacitor according to Claim 1 wherein said capacitor is included in an integrated circuit.
- 9. A ferroelectric capacitor according to 5 Claim 1 further comprising a substrate on said first layer opposite said second layer.
- 10. A ferroelectric capacitor according to Claim 9 wherein said substrate comprises one of a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, or a silicon dioxide layer on a silicon layer.
 - 11. A ferroelectric capacitor comprising:
 a first layer comprising a metal;
- a second layer on said first layer, said second layer comprising a conductive metal oxide wherein said second layer is in the range of 150 to 200 Angstroms thick;
- a third layer on said second layer opposite 20 said first layer, said third layer comprising a ferroelectric material; and
 - a fourth layer on said third layer opposite said second layer, said fourth layer comprising a conductive material.
- 25 12. A ferroelectric capacitor according to Claim 11 wherein said conductive metal oxide comprises one of ruthenium oxide, iridium oxide, lanthanum strontium cobalt oxide, indium tin oxide, or yttrium barium copper oxide.
- 30 13. A ferroelectric capacitor according to Claim 11 wherein said metal comprises a noble metal.

- 14. A ferroelectric capacitor according to Claim 13 wherein said noble metal comprises platinum.
- 15. A ferroelectric capacitor according to Claim 11 wherein said conductive material comprises a conductive oxide.
 - 16. A ferroelectric capacitor according to Claim 11 wherein said ferroelectric material comprises lead zirconate titanate.
- 17. A ferroelectric capacitor according to 10 Claim 11 wherein said capacitor is included in an integrated circuit.
 - 18. A ferroelectric capacitor according to Claim 11 further comprising a substrate on said first layer opposite said second layer.
- 19. A ferroelectric capacitor according to Claim 18 wherein said substrate comprises one of a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, or a silicon dioxide layer on a silicon layer.
 - 20. A ferroelectric capacitor comprising:
 - a first layer comprising a mixture of a conductive metal oxide and a noble metal;
- a second layer on said first layer, said second layer comprising a ferroelectric material; and
 - a third layer on said second layer opposite said first layer, said third layer comprising a conductive material.

-26-

- 21. A ferroelectric capacitor according to Claim 20 wherein said conductive metal oxide comprises one of ruthenium oxide, iridium oxide, lanthanum strontium cobalt oxide, indium tin oxide, or yttrium barium copper oxide.
 - 22. A ferroelectric capacitor according to Claim 20 wherein said noble metal comprises platinum.
- 23. A ferroelectric capacitor according to Claim 22 wherein said first layer comprises less than about 50 atomic percent platinum.
 - 24. A ferroelectric capacitor according to Claim 20 wherein said conductive material comprises a conductive oxide.
- 25. A ferroelectric capacitor according to 15 Claim 20 wherein said ferroelectric material comprises lead zirconate titanate.
 - 26. A ferroelectric capacitor according to Claim 20 wherein said capacitor is part of an integrated circuit.
- 27. A ferroelectric capacitor according to Claim 20 further comprising a substrate on said first layer opposite said second layer.
- 28. A ferroelectric capacitor according to Claim 27 wherein said substrate comprises one of a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, or a silicon dioxide layer on a silicon layer.

- 29. A ferroelectric capacitor comprising:
- a first layer comprising a plurality of alternating interlayers, at least one of said alternating interlayers comprising a first metal, and another of said interlayers comprising one of a second metal and a conducting oxide;
 - a second layer on said first layer, said second layer comprising a ferroelectric material; and
- a third layer on said second layer opposite 10 said first layer, said third layer comprising a conductive material.
- 30. A ferroelectric capacitor according to Claim 29 wherein at least one of said alternating interlayers comprises a noble metal, and another of said interlayers comprises one of ruthenium, iridium, ruthenium oxide, iridium oxide, lanthanum strontium cobalt oxide, indium tin oxide, or yttrium barium copper oxide.
- 31. A ferroelectric capacitor according to 20 Claim 29 wherein said conductive material comprises a conductive oxide.
 - 32. A ferroelectric capacitor according to Claim 29 wherein said ferroelectric material comprises lead zirconate titanate.
- 25 33. A ferroelectric capacitor according to Claim 29 wherein said capacitor is included in an integrated circuit.
 - 34. A ferroelectric capacitor according to Claim 29 further comprising a substrate on said first layer opposite said second layer.

-28-

35. A ferroelectric capacitor according to Claim 34 wherein said substrate comprises one of a silicon layer, a silicon dioxide layer, a magnesium oxide layer, a sapphire layer, a silicon carbide layer, a gallium arsenide layer, or a silicon dioxide layer on a silicon layer.

- 36. A ferroelectric capacitor according to Claim 29 further comprising a primary layer on said first layer opposite said second layer, said primary layer to comprising a primary metal.
 - 37. A ferroelectric capacitor according to Claim 36 wherein said primary metal comprises a noble metal.
- 38. A ferroelectric capacitor according to 15 Claim 37 wherein said noble metal comprises platinum.
 - 39. A ferroelectric capacitor comprising: a first layer comprising a metal;
 - a second layer on said first layer, said second layer comprising a conductive metal oxide;
- a third layer on said second layer opposite said first layer, said third layer comprising a ferroelectric material; and
- a fourth layer on and in direct contact with said third layer opposite said second layer, said fourth 25 layer comprising said conductive metal oxide.
- 40. A ferroelectric capacitor according to Claim 39 wherein said conductive metal oxide comprises one of ruthenium oxide, iridium oxide, lanthanum strontium cobalt oxide, indium tin oxide, or yttrium barium copper oxide.

PCT/US95/16853

- 41. A ferroelectric capacitor according to Claim 39 wherein said metal comprises a noble metal.
- 42. A ferroelectric capacitor according to Claim 39 wherein said noble metal comprises platinum.
- 5 43. A ferroelectric capacitor according to Claim 39 wherein said ferroelectric material comprises lead zirconate titanate.
- 44. A ferroelectric capacitor according to Claim 39 wherein said capacitor is included in an integrated circuit.
 - 45. A ferroelectric capacitor according to Claim 39 further comprising a substrate on said first layer opposite said second layer.
- 46. A ferroelectric capacitor according to
 15 Claim 45 wherein said substrate comprises one of a
 silicon layer, a silicon dioxide layer, a magnesium oxide
 layer, a sapphire layer, a silicon carbide layer, a
 gallium arsenide layer, or a silicon dioxide layer on a
 silicon layer.

1/6

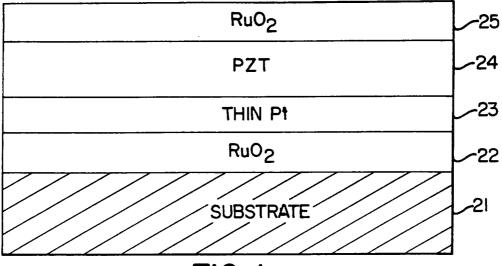


FIG. la.

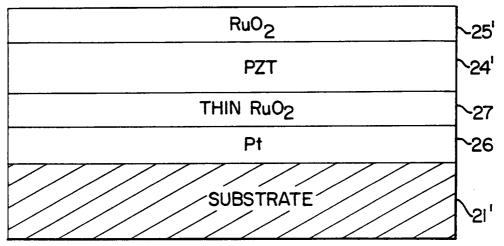


FIG. 1b.

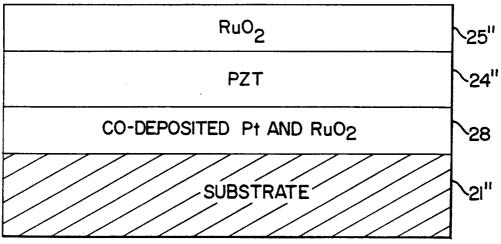
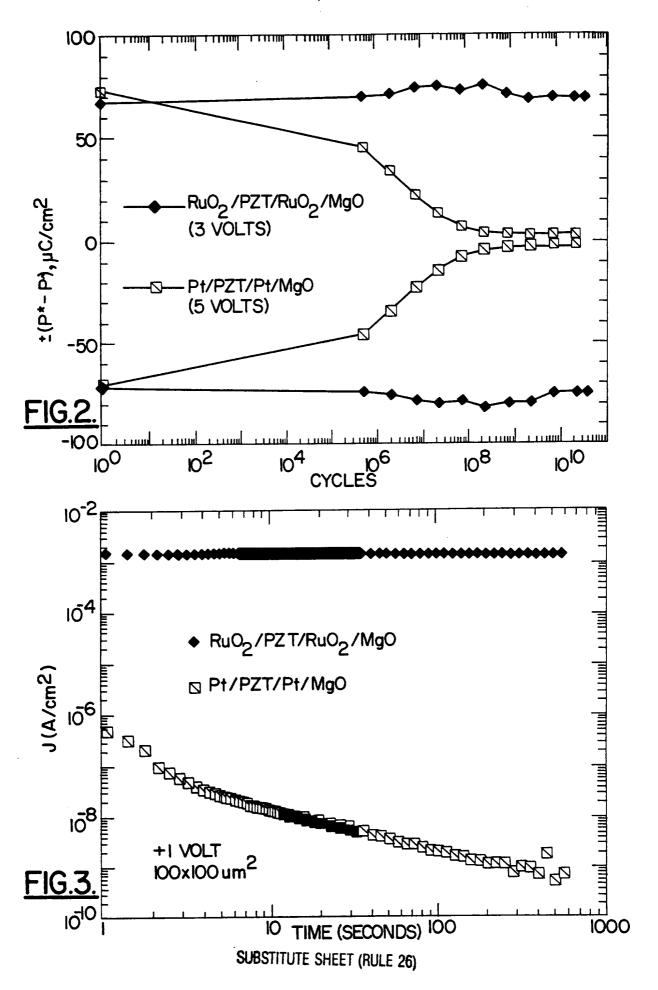
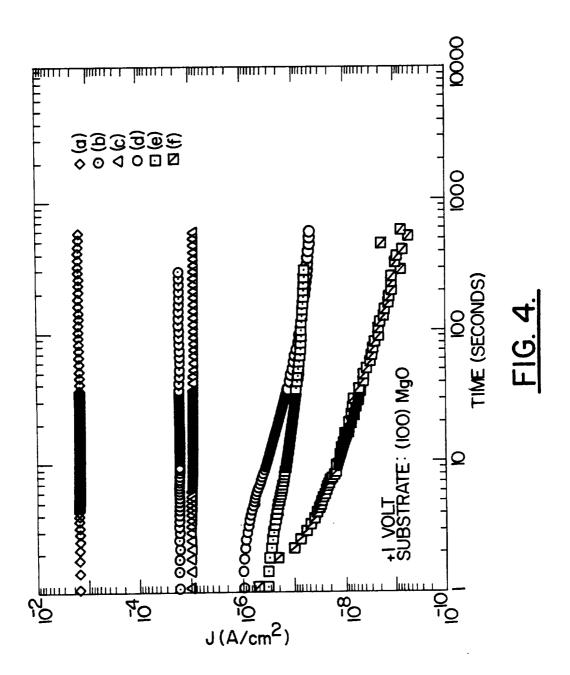


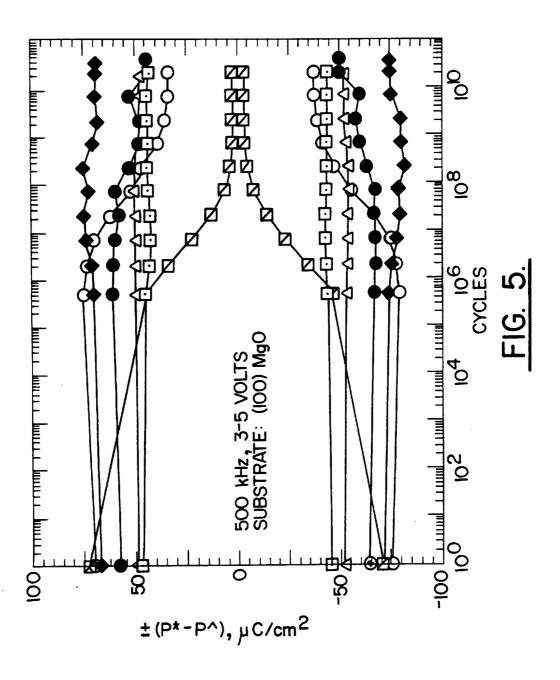
FIG. lc.

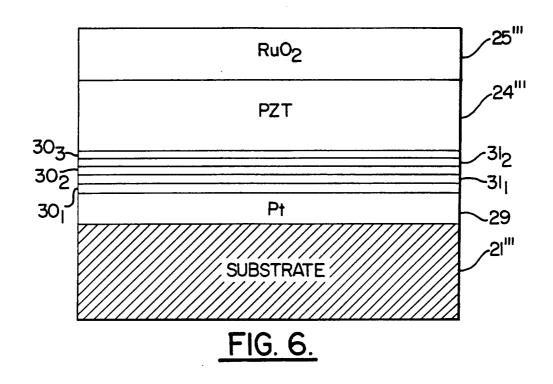
SUBSTITUTE SHEET (RULE 26)

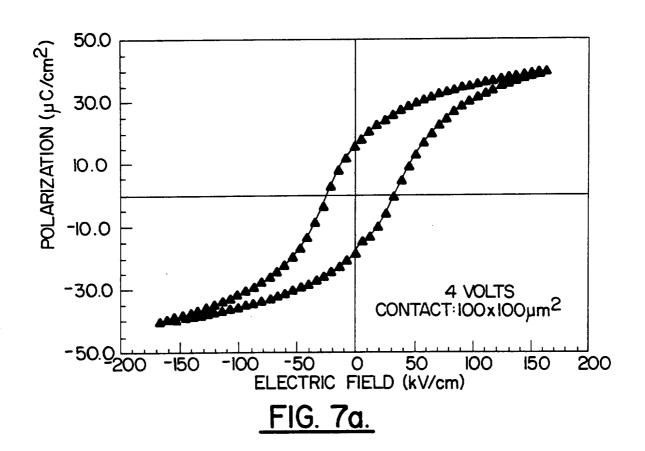




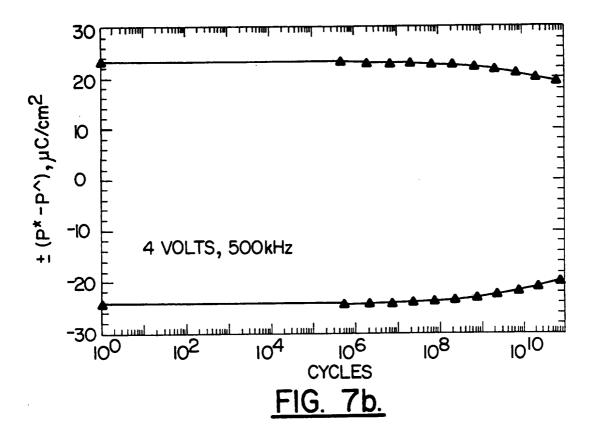


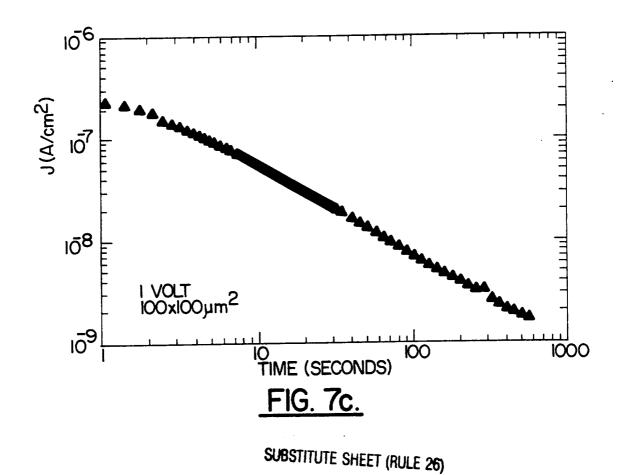






SUBSTITUTE SHEET (RULE 26)





INTERNATIONAL SEARCH REPORT

International application No. PCT/US95/16853

A. CLASSIFICATION OF SUBJECT MATTER								
IPC(6) : H01L 29/00 29/40, 29/49, 29/51;H01G 4/005, 4/008, 4/018, 4/33 US CL : Please See Extra Sheet.								
According to	o International Patent Classification (IPC) or to both i	national classification and IPC						
B. FIELDS SEARCHED								
	ocumentation searched (classification system followed							
U.S. : 2	257/295, 296, 300, 303, 304, 310, 352; 361/305, 313	3, 311, 321, 312						
Documentat	tion searched other than minimum documentation to the	extent that such documents are included	in the fields searched					
Electronic d	lata base consulted during the international search (na	me of data base and, where practicable,	search terms used)					
APS	·							
C. DOC	UMENTS CONSIDERED TO BE RELEVANT							
Category*	Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.					
	US, A, 5,142,437 (KAMMERDIN		1-8, 11-17, 29-					
×	1992, col. 2, lines 58-68; col. 3, li	ines 1-40	33, 36-38					
Υ	, , , , , , , , , , , , , , , , , , ,							
		·	18-19,43					
x	US, A, 5,262,920 (SAKUMA ET	AI) 16 November 1993.	1,9-10,29,34-					
	col. 4, lines 60-68	712/ 10 11000111201	35,39-42,44-46					
Υ	.,							
			18-19-43					
ļ								
		,						
			·					
Furth	l her documents are listed in the continuation of Box C	. See patent family annex.						
	pecial categories of cited documents:	"T" later document nublished after the int	ernational filing date or priority					
"A" document defining the general state of the art which is not considered to be of particular relevance		date and not in conflict with the applic principle or theory underlying the inv	rention					
-E- ea	rlier document published on or after the international filing date	"X" document of particular relevance; the considered novel or cannot be considered novel or cannot be considered.	ne claimed invention cannot be ered to involve an inventive step					
cit	ocument which may throw doubts on priority claim(s) or which is ted to establish the publication date of another citation or other	when the document is taken alone "Y" document of particular relevance; the	ne claimed invention cannot be					
•	ecial reason (as specified) ocument referring to an oral disclosure, use, exhibition or other	considered to involve an inventive combined with one or more other suc	e step when the document is the documents, such combination					
m	eans comment published prior to the international filing date but later than	being obvious to a person skilled in to document member of the same paten						
th	e priority date claimed	Date of mailing of the international search report						
Date of the actual completion of the international search 07 MARCH 1996		21 MAR 1996						
		Authorized officer	. 1-0 - [
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT		ANTHONY DINKINS	- Just 1					
Washington, D.C. 20231 Facsimile No. (703) 305-3230		Telephone No. (703) 308-1782	ist in the second					
i racsimile [TU. (103) 303-3230	<u> </u>						

INTERNATIONAL SEARCH REPORT

International application No. PCT/US95/16853

A. CLASSIFICATION OF SUBJECT MATTER: US CL:							
257/295, 296, 300, 303, 304, 310, 352; 361/305, 313, 311, 321, 312							

Form PCT/ISA/210 (extra sheet)(July 1992)★