

REPORT DOCUMENTATION

AD-A255 358



1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE Jul 92	3. REPORT TYPE AND DATES COVERED Final 1 Jun 89-31 May 92
----------------------------------	--------------------------	--------------------------------------------------------------

4. TITLE AND SUBTITLE Reliability of Sol-Gel Derived Ferroelectric Memories	5. FUNDING NUMBERS DAAL03-89-K-0104
--------------------------------------------------------------------------------	----------------------------------------

6. AUTHOR(S) Sandwip K. Dey

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(S) Arizona State University Tempe, AZ 85287	8. PERFORMING ORGANIZATION REPORT NUMBER
--------------------------------------------------------------------------------------------------	------------------------------------------

DTIC
SELECTED
SEP 08 1992

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 26827.7-PH
-----------------------------------------------------------------------------------------------------------------------------------------------------	--------------------------------------------------------------------

11. SUPPLEMENTARY NOTES
The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12b. DISTRIBUTION CODE
----------------------------------------------------------------------------------------------------	------------------------

13. ABSTRACT (Maximum 200 words)

A process was developed to prepare PZT(52/48) precursor solutions. Five spin-on depositions of this solution (0.5M) were necessary to grow 0.5 μm thin films of polycrystalline PZT onto PT passivated silicon wafers. An addition of 15% excess PbO aided the densification process. Films derived from 1.5M solutions resulted in PZT films of equivalent thickness in only two depositions.

Dielectric constant and $\tan\delta$ were 800 and 2% respectively, at 1 kHz. Remnant and saturation polarizations were 12 and 25 $\mu\text{C}/\text{cm}^2$, respectively. Coercive fields of 36-48 kV/cm were measured. From retention experiments, a polarization loss of 11.2% after 3.2 years was estimated (i.e., the switched charge would diminish from 5.8 to 5.2 $\mu\text{C}/\text{cm}^2$). High frequency pulse fatigue data on Nb and Sn modified PZT showed a reduction of the switched charge of 26% after 4×10^{12} polarization reversals.

92 9 02 100

92-24384



14. SUBJECT TERMS Sol-Gel processing; fatigue; retention; ferroelectric thin films, memories	16. PRICE CODE 7
-------------------------------------------------------------------------------------------------	---------------------

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL
-------------------------------------------------------	----------------------------------------------------------	---------------------------------------------------------	----------------------------------

FINAL PROGRESS REPORT

1. PROPOSAL NUMBER: 26827-PH
2. PERIOD COVERED BY REPORT: JULY 1, 1989 TO JUNE 30, 1992
3. TITLE OF PROPOSAL: RELIABILITY OF SOL-GEL DERIVED FERROELECTRIC MEMORIES
4. CONTRACT OR GRANT NUMBER: DAALO3-89-K-0104
5. NAME OF INSTITUTION: ARIZONA STATE UNIVERSITY
6. AUTHOR OF PROGRESS REPORT: PROFESSOR SANDWIP K. DEY
7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP DURING THIS PERIOD, INCLUDING JOURNAL REFERENCES:
Please see page two of this report.
8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS PERIOD:
Mr. Anjaneya R. Modak (MS degree granted)
Mr. Arup Gupta (MS degree granted)
Mr. Ming-Yi Lee
Mr. P. Coffman
Prof. Sandwip K. Dey
9. REPORT OF INVENTIONS
None

Sandwip K. Dey
Department of Chemical, Bio and Materials Engineering
Arizona State University
Tempe, Arizona 85287-6006

**Item 7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO
SPONSHORSHIP DURING THIS PERIOD**

- 1) "Sol-Gel Processing and Characterization of Ferroelectric PZT Thin Films," A.R. Modak and S.K. Dey, in Ceramic Transactions, vol. 15, 477, Materials and Processes for Microelectronic Systems, eds. K.M. Nair, R. Pohanka and R.C. Buchanan, 1990.
- 2) "Advances in Perovskite Thin Films: Chemical Processing, Properties, and Electrical Applications," S.K. Dey, Fifth U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Kyoto, Japan, December 12-14, 1990.
- 3) "Properties of Ferroelectric PZT Thin Films From High Molarity Polymeric Precursor Solutions," A. Gupta and S.K. Dey, in Ferroelectric Films, Eds. A.S. Bhalla and K.M. Nair, *Ceramic Transactions*, The American Ceramic Society, **25**, 243-250 (1992).
- 4) "Nanostructure Evolution During the Transition of TiO_2 , $PbTiO_3$, and PZT From Gels to Crystalline Thin Films," Z.C. Kang, A. Gupta, M.J. McKelvy, L. Eyring and S.K. Dey. *Mater. Res. Symp. Proc.*, **230**, 301 (1992).
- 5) "Preliminary Observations on Ferroelectric $Pb(Zr_xTi_{1-x})O_3$ Thin Films With Excess Lead," S. K. Dey and A.R. Modak, sent to the Journal of the American Ceramic Society, December 1991.
- 6) "Transmission Electron Microscopy Observations of Sol-Gel Derived Ferroelectric $PbZrO_3$ - $PbTiO_3$ Thin Films," A.R. Modak and S.K. Dey, *Ferroelectrics* (in press), Nov. 1991.
- 7) "Early Evolutionary Stages of Condensation and Crystallization in Acid and Base Catalyzed $PbZrO_3$ - $PbTiO_3$ Gels: A High-Resolution Electron Microscopic Study," Z.C. Kang, S.K. Dey and L. Eyring, *Mater. Res. Symp. Proc.*, **183**, 291 (1990).
- 8) "The Effect of Ionizing Radiation on Sol-Gel Ferroelectric PZT Capacitors," J.M. Benedetto, R.A. Moore, F.B. McLean, P.S. Brody and S.K. Dey, *IEEE Trans. Nucl. Sci.*, **NS-37**[6], 1713 (1990).

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
Dist	Special
A-1	

BRIEF OUTLINE OF RESEARCH FINDINGS

The need for integrated ferroelectrics have led to progress in understanding of: a) organometallic precursor synthesis, b) thin film fabrication, c) evolution of the structure, and d) interfacial and radiation effects, and their influences on electrical and optical properties. Research efforts in our group, under the present ARO contract, focused on the thin film chemical processing technique of solution-gelation (sol-gel), and the electrical characterization of ferroelectric capacitor structures made thereby. In the process of such efforts, dense and crack-free ferroelectric $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ or PZT (52/48) thin-films ($0.5\mu\text{m}$ thick) were integrated onto Pt/Ti/SiO₂/(100)Si wafers (3 inch diameter). Dense perovskite microstructures were obtained at temperatures as low as 550°C within 15 minutes. These films exhibited remnant polarization (P_r), maximum polarization (P_{max}), and coercive field (E_c) in the range of $29\text{-}32\ \mu\text{C}/\text{cm}^2$, $44\text{-}53\ \mu\text{C}/\text{cm}^2$ and $50\text{-}60\ \text{kV}/\text{cm}$, respectively. Recent studies of high speed ferroelectric perovskite switching times $<2.7\text{ns}$ were measured on $19\times 19\ \mu\text{m}^2$ capacitors. Measurements made on $2.5\times 2.5\ \mu\text{m}^2$ $\text{Pb}(\text{Nb,Zr,Sn,Ti})\text{O}_3$ thin film capacitors gave sub-nanosecond switching times. These measurements were, however, circuit limited and were not representative of the intrinsic switching time. Interestingly, independent preliminary TEM studies on perovskite thin film samples under an applied (*in-situ*) dc-bias indicate that domain nucleation occurs at domain walls. If this result in indeed the general case, it is possible that single crystals may switch polarization more slowly than polycrystalline thin films of the same composition. Thus, future observations of intrinsic switching times (in polycrystalline films) in the 10's of picoseconds may not be surprising.

In PZT, the relaxation of internal strains through the ferroelastic effect can reorient 90° domains. This in turn, causes a retention (of the polarization) problem well below the Curie temperature. It is therefore, necessary to fabricate dense PZT films with a minimal unit cell distortion in order to improve retention performance. Figure 1 illustrates reproducible retention behavior of a $42\times 42\ \mu\text{m}^2$ Nb-modified PZT(52/48) thin film ($0.5\mu\text{m}$ thick) capacitor. The charge retention was characterized by measuring the polarization after a delay (since poling the capacitor into a known state) with no intervening voltage applications. The non-switching (n_s) charge remains constant while the full-switching (f_s) charge exhibits a small negative slope after 2.8 days (or 10^3s). The difference ($f_s - n_s$), i.e., the retained polarization that switched (S), is 93%. Assuming that the switched charge versus delay time continues to obey this logarithmic dependence, the loss of polarization (extrapolated to 3.2 years) will be 11.2%, i.e., the retained charge will change from 5.8 to $5.15\ \mu\text{C}/\text{cm}^2$. In the future, additional processes or mechanisms that limit such retention performance must be identified and controlled in integrated devices.

Early results on low frequency sinusoidal fatigue measurements on thin films indicated that compositions near the morphotropic phase boundary, i.e., PZT(52/48), are most promising. High frequency pulse fatigue measurements have demonstrated a similar trend. Figure 2 illustrates promising fatigue results of a Nb and Sn modified $42\times 42\ \mu\text{m}^2$ PZT thin film ($0.6\ \mu\text{m}$ thick) capacitor. The rise time, amplitude, pulse width, and bipolar pulse frequency of this polarization reversals study was 1ns , 4V , 33ns , and $7.1\ \text{MHz}$, respectively. Again, a major

challenge ahead will be to demonstrate such performances in integrated ferroelectric memory devices.

Major Achievements

The following is a compilation of major accomplishments for the three years duration of this research project.

- A process was developed to prepare PZT(52/48) precursor solution.
- Crack-free PZT(52/48) thin films were successfully deposited onto 3 inch Pt- passivated silicon wafers. Five consecutive depositions were necessary to obtain a thickness of 0.5 μm .
- The addition of 15 mole% of excess lead (PbO) was found to densify (elimination of porosity) the thin films.
- Ferroelectric domains in 90° arrays were first observed in these films by TEM.
- A simplified process for the fabrication of ferroelectric PZT thin films, by a reduced number of deposition steps of a high molarity polymeric precursor solution was developed.
- Crack-free, dense microstructure films (0.5 μm thick) were successfully obtained by only two depositions.
- HREM observation of the structure evolution of the final perovskite phase was made on thin films from PZT and PT precursor gels, obtained by acid and base catalyzed hydrolysis.
- The presence of acetate groups in the gel, due to the incomplete exchange of lead acetate with 2-methoxyethanol, was verified by FTIR.
- The mechanism of acetate decomposition, to the oxide, appeared to be via the carbonate intermediate, with the evolution of acetone and carbon dioxide. The acetate does not decompose completely and increases the organic content in the fired product.
- Combination of ^1H NMR and ^{13}C NMR analytical techniques indicated the presence of residual acetate species in the hydrolyzed solution. The slight presence of acetates made the PZT(52/48) precursor solution more difficult to hydrolyze.
- X-ray diffraction studies showed the formation of phase pure perovskite only in a PZT(52/48) film (0.45 μm thick), made by two deposition steps of a 1.15M precursor solution. The dielectric constant and $\tan \delta$ were 800 and 2% respectively, at 1 kHz. Remnant polarization and saturation

polarization values of 12 and 25 $\mu\text{C}/\text{cm}^2$ respectively, were measured, at coercive field values of 36-48 kV/cm.

- Sol-gel solid phase epitaxial growth of (110) PNZT on 3 inch diameter (0112) Sapphire was confirmed by HRTEM and x-ray analyses.

- The films were 0.6 μm thick, transparent in the 0.5-5.6 μm wavelength range, had a refractive index of 2.5-2.6 (at 0.6328 μm) and an optical band gap of 3.63 eV.

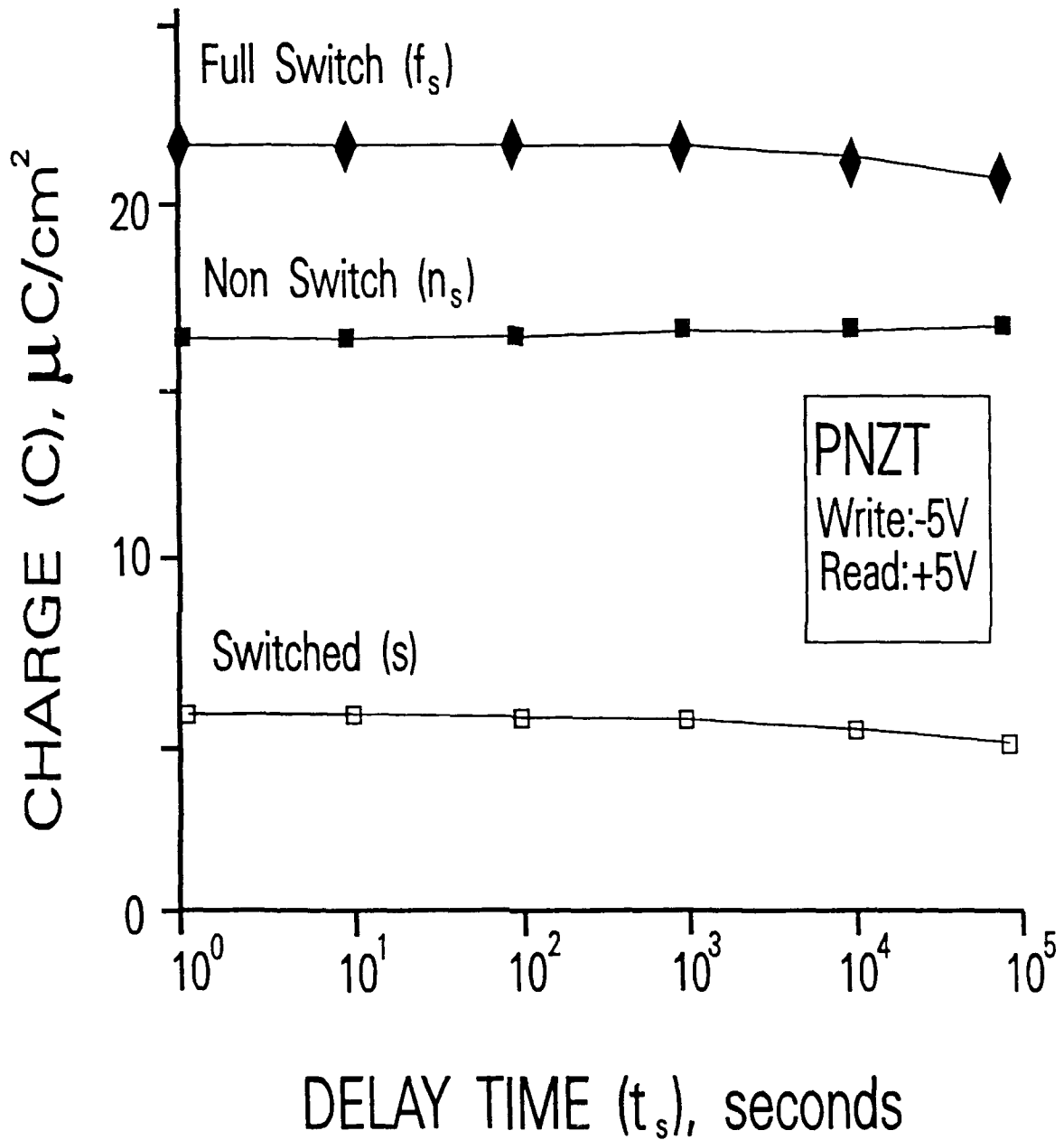


FIGURE 1

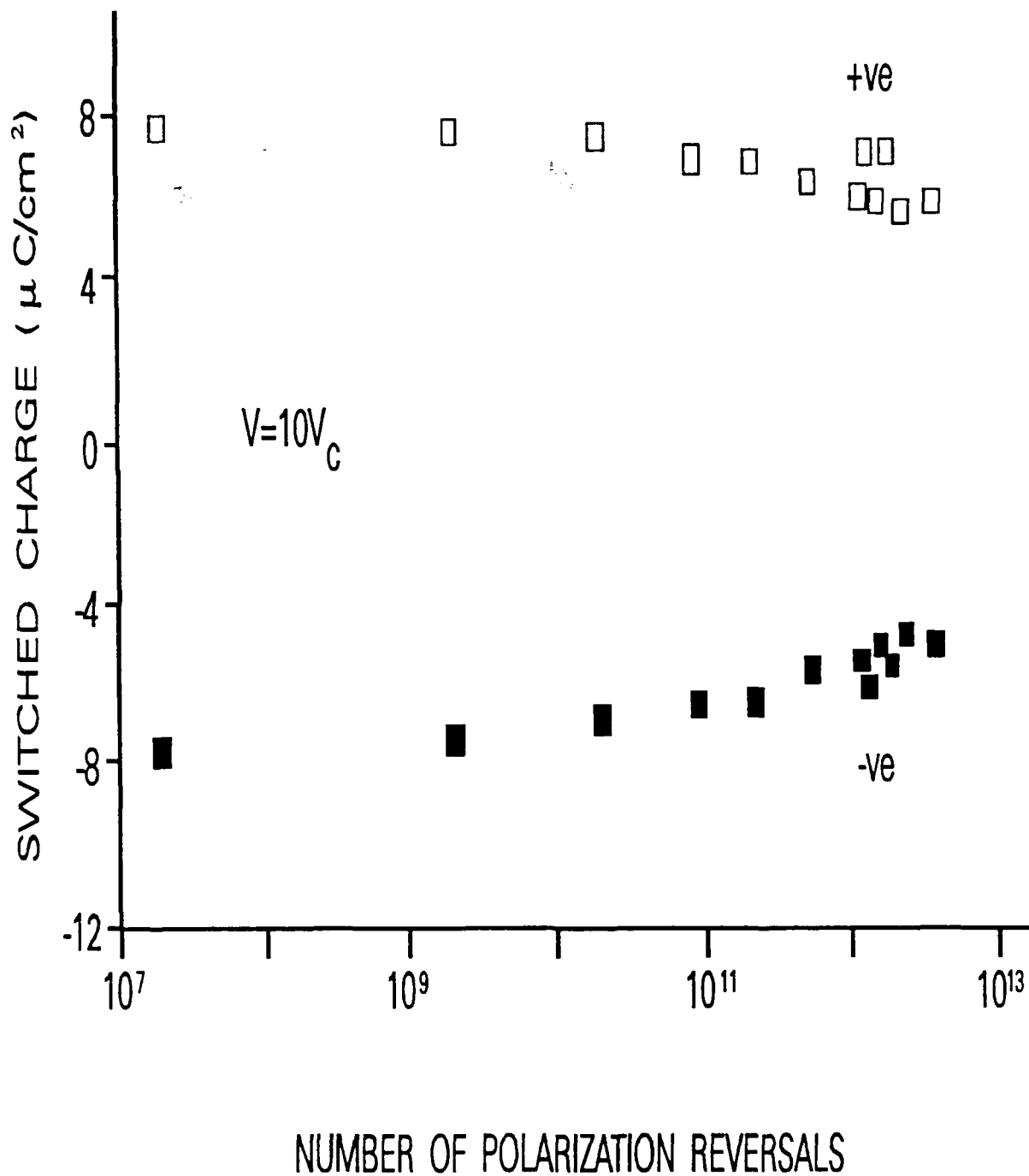


FIGURE 2