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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 tanδ were 800 and 2% respectively, at 1 kHz. Remnant and saturation polarizations were 12 and 25 μC/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 μC/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.

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6. AUTHOR OF PROGRESS REPORT: PROFESSOR SANDWIP K. DEY

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   Please see page two of this report.

8. SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT AND DEGREES AWARDED DURING THIS PERIOD:
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   Mr. Arup Gupta (MS degree granted)
   Mr. Ming-Yi Lee
   Mr. P. Coffman
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9. REPORT OF INVENTIONS
   None

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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).

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 $Pb(Zr_{0.52}Ti_{0.48})O_3$ or PZT (52/48) thin-films (0.5μm thick) were integrated onto $Pt/Ti/SiO_2/(100)Si$ 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 29-32 $\mu C/cm^2$, 44-53 $\mu C/cm^2$ and 50-60 kV/cm, respectively. Recent studies of high speed ferroelectric perovskite switching times <2.7ns were measured on 19x19 μm^2 capacitors. Measurements made on 2.5x2.5 μm^2 $Pb(Nb,Zr,Sn,Ti)O_3$ 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 42x42 μm^2 Nb-modified PZT(52/48) thin film (0.5μm 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 10^5s). 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 $\mu C/cm^2$. 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 42x42 μm^2 PZT thin film (0.6 μm thick) capacitor. The rise time, amplitude, pulse width, and bipolar pulse frequency of this polarization reversals study was 1ns, 4V, 33ns, and 7.1 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 ^{1}H 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 δ were 800 and 2% respectively, at 1 kHz. Remanant polarization and saturation polarization values of 12 and 25 μC/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.

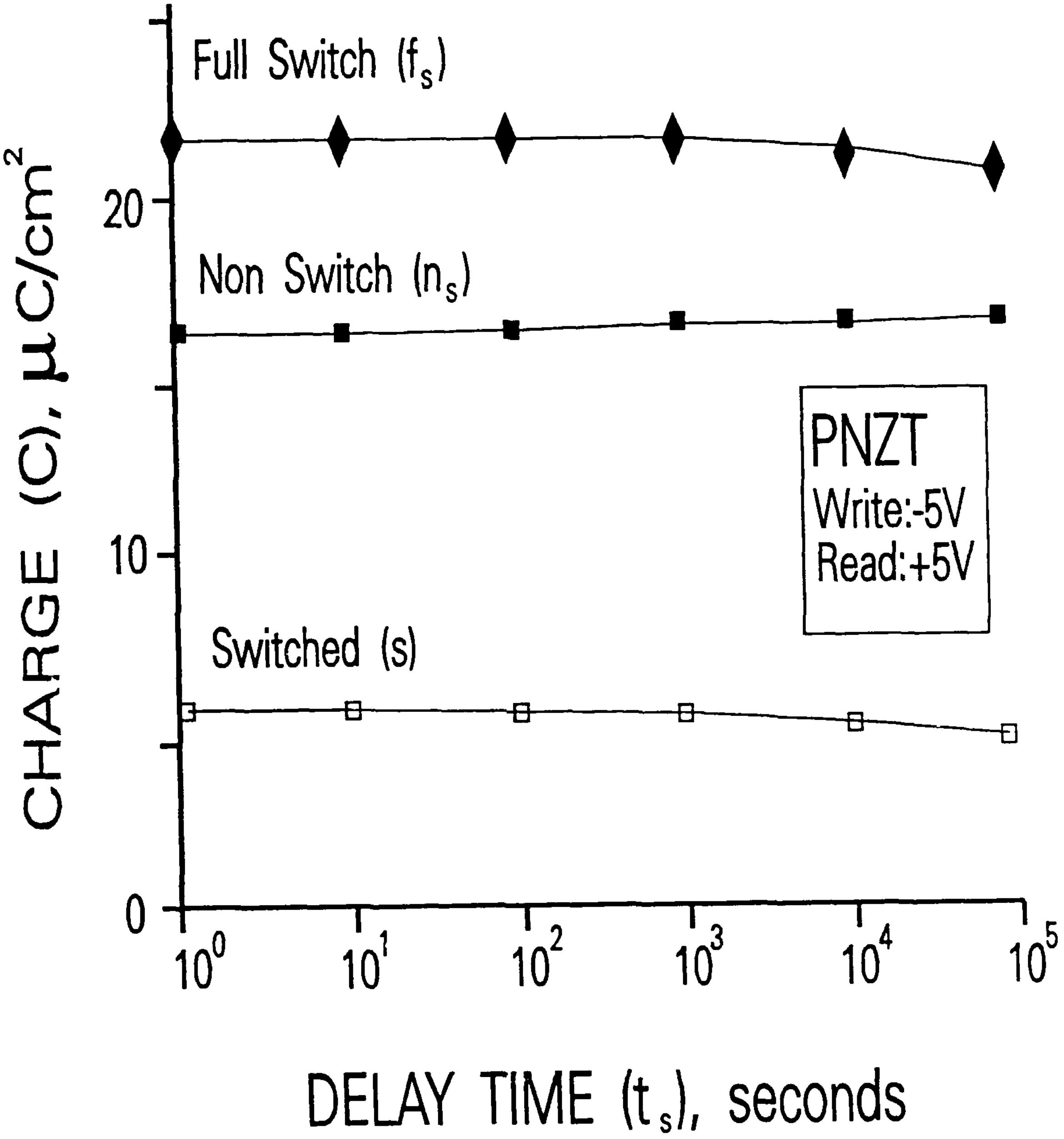
Full Switch (f_s)
Non Switch (n_s)
Switched (s)
PNZT
Write:-5V
Read:+5V
CHARGE (C), μC/cm^2
0
10
20
10^0
10^1
10^2
10^3
10^4
10^5
DELAY TIME (t_s), seconds

FIGURE 1

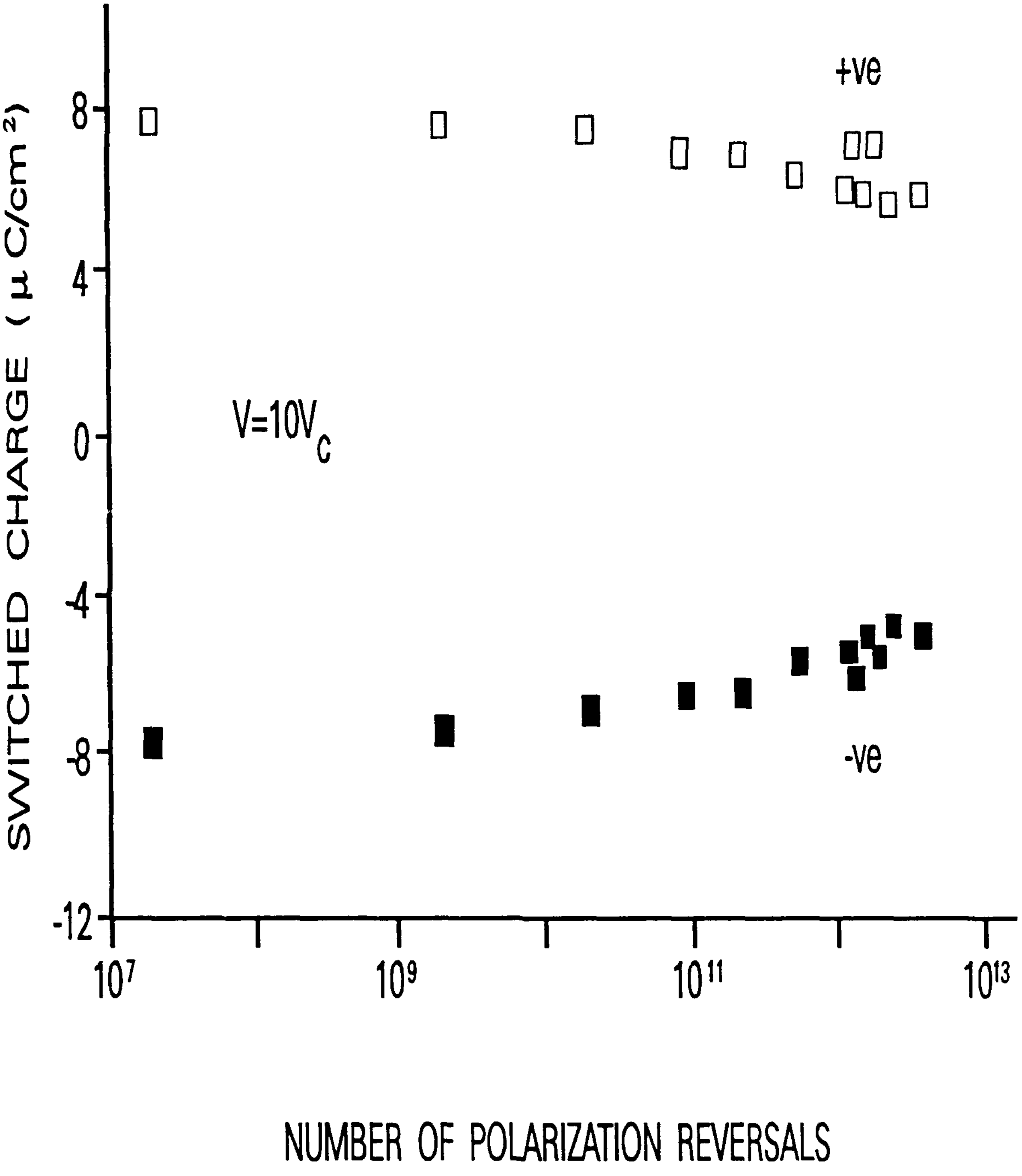
SWITCHED CHARGE (μ C/cm²)
8
4
0
-4
-8
-12
+ve
-ve
V=10V$_c$
10⁷
10⁹
10¹¹
10¹³
NUMBER OF POLARIZATION REVERSALS

FIGURE 2