**Title:** Studies of structure and switching dynamics in ferroelectric crystal and liquid crystal thin films (Unclassified)

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**Abstract:**

The structure and switching dynamics of ferroelectric solid state and liquid crystal thin films were investigated experimentally using x-ray scattering, optical microscopy and microspectroscopy, and by raman spectroscopy. Applications of crystalline piezoelectric ferroelectric films, formed by sol-gel and sputter deposition and ferroelectric liquid crystal devices were studied for application.
1 Introduction

1.1 This Report

This report describes work done under ARO Contract DAAL03-86-K-0053 which has funded research on high speed solid state and liquid crystal electro-optic switching over the past three years. The principal research direction of this program has been to advance the basic physical understanding of thin film ferroelectric crystal and liquid crystal electro-optic switching, a necessary step if the profound potential of these new technologies is to be realized.

Although the details of the device physics of thin film solid state and liquid crystal ferroelectrics are quite different, they exhibit the following common features which makes their joint study attractive. Firstly, the basic cell structure of a ferroelectric material in a (possibly transparent) capacitor is the same in the two cases, so that the techniques and setups required for structural and dynamical studies are essentially identical, including the optical microscopic, electrical, x-ray, and light scattering experiments. Secondly, these two areas represent new technologies of enormous potential impact which exhibit a variety of unexplained behavior. In both ultra-thin solid state and liquid crystal films, surface interactions, finite size mechanical effects, electrostatic effects, and structural variations combine to produce a variety of novel physical phenomena which remain almost totally unexplored and are not well understood. It is this lack of understanding that rates limits the commercialization of these technologies.

1.2 Ferroelectric Thin Film Devices

1.2.1 Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) Electro-Optics

The SSFLC electro-optic device concept, invented by one of the co-PIs (NAC), is revolutionizing the electro-optic applications of liquid crystals. SSFLC cells exhibit fast (sub-micro second) electro-optic response, a large electro-optic effect (rotation of a birefringent plate of $\delta n \sim 0.2$ through $45^\circ$) giving high optical contrast, and bistability. SSFLCs are now under intense worldwide development as display devices, photo and electrically addressed spatial light modulators, and electrooptic switches in fiber optic computer and communication applications.

1.2.2 Crystalline Ferroelectric Thin Film (CFTF) Nonvolatile Memories

Thin films of solid state ferroelectric materials deposited on solid substrates are now recognized as the principal new technology for the development of commercially prac-
tical nonvolatile random access memories (RAMs). In addition CFTF memories exhibit the important advantage of radiation hardness, being able to withstand dose rates of $> 10^{11} \text{Rad/cm}^2\text{sec}$, and net doses of $> 5 \times 10^{9} \text{Rad/cm}^2$ (1MeV gammas) or $10^{14}$ neutrons/cm$^2$ and exhibit no single event upset.

2 Work Under the Previous Contract Period

2.1 Previous Contract Period Work: Highlights

Experimental and/or theoretical work has been carried out in the following areas:

* Optical microscopy, laser reflectivity, x-ray scattering, and theoretical studies of SS-FLC cells.

* Laser Raman scattering, electrical measurements, fabrication technique development, and radiation studies of CFTF cells.

Highlights of accomplishments under the previous grant period are:

* Discovery of an efficient technique to restore fatigued crystalline ferroelectric thin film (CFTF) memories to their virgin condition (APPENDIX I).

* Discovery of the novel "chevron" layer structure in surface stabilized ferroelectric liquid crystal (SSFLC) cells (APPENDIX II).

* Complete geometrical characterization of the principal SSFLC optical contrast degrading defect, enabling high contrast cells to be made (APPENDIX III).

* Demonstration that charge retention failure in CFTF memories can be avoided by open circuiting unaddressed cells (APPENDIX IV).

* Direct demonstration by laser total internal reflection of surface switching in SSFLC devices (APPENDIX V).

* Demonstration that the phase diagram of CFTFs is qualitatively different from the bulk (APPENDICES VI & VII).

* Analysis of SSFLC switching in terms of solitary wave propagation (APPENDIX
VIII).

* Demonstration of an SSFLC matrix array with record high spatial resolution (APPENDIX IX).

* Analysis of the kinetics of CFTF switching (APPENDIX X).

* Discovery of the anisotropic thermal lens effect near the paraelectric-ferroelectric transition in $Ba_2NaNb_5O_{15}$.

2.2 Previous Contract Period Work: Details

2.2.1 Crystal Ferroelectric Thin Films

In the initial phase of this contract, we emphasized the detailed analysis of optical and electrical properties of $KN0_3$ thin film memories. This was in part because potassium nitrate memories can be prepared by thermal evaporation with extremely high crystallinity and stoichiometry; such films are also exceptionally fast, switching in 10ns or less at voltages of order 5V, compatible with integration into standard silicon CMOS devices. However, due to the extreme water sensitivity of this material at every step of fabrication, the consensus in the ferroelectrics community is that initial fabrication of commercial devices will employ PZT (lead zirconate titanate). Therefore, in the second year of our research program, we shifted emphasis to this material. In the study of both these thin film materials, we have provided fundamental understanding of computer memory devices of commercial and military importance.

We performed a series of optical (laser Raman spectroscopy) and electrical (current transient shapes $i(t)$ and hysteresis curves) measurements on ferroelectric thin films in the attempt to understand their kinetics as fast switching memory devices. We also found that the bulk phase diagrams were significantly altered by finite size effects; thin films can have phase boundaries as much as $70K$ higher than in bulk (APPENDICES IV & VII, P13, 19). In some cases (e.g., $KNO_3$ ferroelectric films), we were able to demonstrate that this occurs due to surface electric fields and not due to film-substrate interfacial strain. This effect is most notable in the case of $KNO_3$, where the ferroelectric phase is stable over a temperature range of only a few degrees, from $117 - 125^\circ C$; whereas in 70nm thin-films, it is stable from $-200^\circ C$ to $+196^\circ C$ (see figure 3 of APPENDIX VII). Such an increase in the Curie temperature ($125$ to $196^\circ C$) with decreasing thickness is compatible with

1 references denoted by $P#$ refer to the list of publications under the previous grant period on pages 9-11
he theories of Lubensky and Rubin[1] and of Tilley and Zeks[2]. Annealing experiments show that this effect is not due to stress at the ferroelectric interface but an electrical property related to similar size effects in small particles[3]. Similar thickness effects have been reported in other ferroelectrics, notable in the TGS work by Hadni et al.[4] and related surface charge mechanisms have been described in ferroelectric thiourea by Farhi and Moch[5]. Our observations have been independently verified by Seffer and Mikola[6].

We have shown (APPENDIX X, P15) that the switching kinetics in ferroelectric thin films can be described by Ishibashi’s theory[7]. In particular, the rate-limiting step in domain switching is the sideways growth of domains in the plane of the film. The theory describes both unirradiated and irradiated films and shows that irradiated films exhibit switching kinetics that are more one-dimensional, with needle-like domains propagating normal to the film surface dominating the post-irradiation kinetics. To our knowledge, our data are the only detailed switching data to be published on irradiated ferroelectric devices.

We discovered an efficient way to restore fatigued ferroelectric thin film memories to their virgin condition (APPENDIX I, P21): By applying a single 30$\mu$s voltage pulse that is approximately 300% of the normal switching pulse (e.g., 15V in a nominally 5V CMOS integrated circuit), one can de-pin domains walls that have become pinned at grain boundaries or other defects and restore the memory cell to its initial switched charge ($P_s$) value and to its original speed. This technique works in KNO$_3$ films and in sol-gel PZT films. It does not work in rf-sputtered PZT, presumably because the lower stoichiometry in the latter produces higher pinning energies. This technique may result in a $10^6$ improvement in the fatigue limits of ferroelectric memories, a point of very high priority at present for military and commercial applications.

We have shown (APPENDIX IV, P20) that if ferroelectric thin-films are irradiated under short-circuited conditions, strong electret effects are possible in which space charge can destroy the retention of the device (i.e., “homocharge” at the electrode interface can reverse the apparent stored polarization $+P_s$, giving a net negative stored charge). Thus, we found that PZT memories undergo significant degradation if and only if they are stored in a short circuited condition. Under such circumstances strong electret-like effects involving free charge excited out of deep traps cause catastrophic loss of retention. Our work shows that this major source of retention-failure in ferroelectric RAMs can be circumvented by a chip architecture that involves storage of un-addressed cells in an open-circuit condition. This is a major improvement in rad-hard characteristics for ferroelectric RAMs. This analysis thus has important implications for the chip architecture of ferroelectric thin-film RAMs. Both total does (5.04MRad) and very high dose rate (2 x $10^{11}$Rad/sec/cm$^2$) were tested. Both KNO$_3$ and PZT devices were examined in this way.
The organization of this work was in the form of a cooperative effort involving the Physics Department of the University of Colorado and personnel from Symetrix Corporation, a small R & D company located in Colorado Springs. Symetrix prepared the ferroelectric films, some of which involved proprietary processing techniques, and performed the irradiation of the films. The University performed most of the analyses and testing of the films. In this way, most of the results are publishable in the open literature and form the bases of graduate student M.S. and/or Ph.D. candidate theses. Mr. Shawabkeh, coauthor of APPENDIX IV, is a Ph.D. candidate in Physics at the University of Colorado whose thesis is based upon this work.

We have performed a series of experiments to analyze a novel scattering process (P23) accidentally discovered in the course of work on ferroelectric barium sodium niobate ($\text{Ba}_2\text{NaNb}_5\text{O}_{15}$). Near $T_c = 838K$ we have discovered an unexpected scattering of laser light into a nearly circular cone of light approximately 11° or arc from directly forward. This ring changes its angle with time and displays unusual polarization characteristics. Initially we thought it was due to a photorefraction involving diffusion of charged ions, but more recently we were able to show that it arises from the thermal lens effect, an effect originally observed only in isotropic liquids. The effect arises because $\frac{dn_c}{dt}$ at $T_c = 838K$ in $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ diverges at $T - T_c$ from below, becoming quite large ($2 \times 10^{-7} \text{K}^{-1}$) exactly at $T_c$ – a value exactly equal in magnitude but opposite in sign from the isotropic value of $\frac{dn}{dT}$ in simple liquids).

We have extended our analyses and fabrication of ultra-fast ferroelectric thin film ferroelectric memories from rf-sputtered PZT to sol-gel PZT and some related wet-chemistry spin-on techniques that use precursors quite different from the usual sol-gel processes; this has produced significant improvements in voids, pin-holes, and microcracks as well as improved fatigue and retention.

2.2.2 Surface Stabilized Ferroelectric Liquid Crystals

Our research has focussed on understanding in full detail the director and layer structure in SSFLC devices. SSFLC cells have ferroelectric smectic C liquid crystal as the dielectric in a transparent capacitor formed by parallel plates spaced by on the order of 1 to 3 microns. The SSFLC geometry exhibits fast, bistable electro-optic effects which are currently under intense, worldwide development for a variety of light control and display applications. A major focus of SSFLC research is on understanding their electro-optical characteristics and on obtaining stably aligned, defect-free cells, since SSFLC cells show a variety of characteristic defects, as shown in Figure 2 of APPENDIX XI, which leak light and reduce bistability. We decided several years ago that the solution to the defect problem
might lie in a better understanding of how the smectic layers organize in SSFLC cells and applied our expertise in x-ray scattering from small volume LC samples to this problem.

The x-ray program has been remarkably successful, the results unveiling the bent layer structure for which we have coined the term “chevron” and have led to a complete understanding of the layer and defect structures for several different surface preparations (APPENDICES II, III & XI, P11, 17, 18). We have shown that the chevron layer structure results from the combination of layer anchoring at the surfaces, absence of dislocations, and the layer shrinkage accompanying director tilt in the SC phase. With these conditions as operating principles, the detailed three dimensional structure of the zig-zag defect can be understood (APPENDIX III).

As a result of our work x-ray characterization of the layer is becoming a standard technique in the preparation and study of Surface Stabilized Ferroelectric Liquid Crystal cells. We showed that it is essential to characterize the SSFLC layer structure if the electro-optic behavior is to be understood. Furthermore, the results point to ways of eliminating defects and have put the whole problem of preparing SSFLC cells on a firm scientific basis.

We have pursued theoretical models aimed at describing and understanding SSFLC switching dynamics. The reorientation $\phi(r,t)$ of the director (n polarization (P) couple is governed by nonlinear differential equations which have been solved either numerically or analytically depending on the situation. For spatially uniform n-P and models having both ferroelectric and dielectric torques, we have generated a series of equations giving the optical response time (10% to 90%) and delay time (0% to 10%), which are now widely used to interpret switching data (P7, 9, 10).

We have solved a series of cases where $\phi$ depends on a single spatial variable. These require numerical solution. The results show a variety of interesting effects, particularly for switching at high field which occurs primarily by the propagation of solitary waves (P1, P14). This work has been compiled into a forty page book chapter (APPENDIX VIII, P1).

Several avenues of prototype device development have been pursued. Of particular importance in optical computing applications are high resolution electrically addressed spatial light modulators composed of two dimensional arrays of individually addressable pixels. We have demonstrated the highest resolution such array yet made (APPENDIX IX, P2). Figure 1 of APPENDIX IX shows a portion of this array, which has pixels which are 17 microns square, spaced by 5 microns. As can be seen the pixel definition is within about 2 microns, showing that arrays with pixel sizes as small as 5 microns square could be made.
In our original invention of the SSFLC geometry [8], we proposed that in these structures bistable behavior was achieved by the surface switching, i.e. by a switching of the surface orientation of n-P stabilized by interface interactions. This claim was made on the basis of the geometry of the n-P field throughout the SSFLC cells, i.e. we did not have a direct probe of the surface. During the past funding period we have carried out a surface probe experiment, using total internal reflection to study the FLC-solid interface (APPENDIX V, P16). The results show that indeed surface switching occurs, with any unswitched layer remaining thinner than 20Å. These measurements enable us to determine the exact boundary condition for input into numerical calculations.

We have constructed a microscope-based spectrophotometer to measure the transmission dependence on wavelength of our SSFLC cells (P9). These data provide a quantitative test of our model calculations. By fitting a transmission spectrum for a particular sample orientation and field and then varying both applied field and sample orientation we have a very sensitive assay of the structure of the n field. For low polarization materials we obtain good fits to our models.
2.3 Publications Supported by the Previous Contract


**P10.** "ELECTROOPTICAL SWITCHING PROPERTIES OF UNIFORM LAYER TILTED


2.4 Ph. D. Theses Supported by the Previous Contract


2.5 Invited Presentations of Work Supported by the Previous Contract


6. “FERROELECTRIC MEMORIES,” J. F. Scott, National Semiconductor (Santa Clara), IBM (Yorktown Heights), United Technologies (East Hartford), General Motors (Warren, Kokomo, Santa Barbara), Harris Semiconductors (Melbourne), Honeywell (Minneapolis).


