

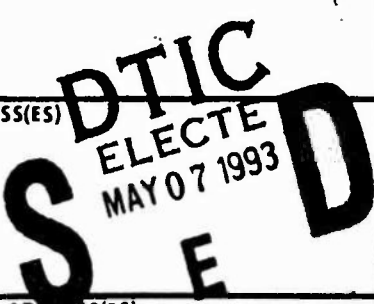

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13. ABSTRACT (Maximum 200 words) The structure and switching dynamics of ferroelectric solid state and liquid crystal thin films were investigated experimentally using x-ray scattering, dielectric measurements, and optical microspectroscopy. Crystalline piezoelectric ferroelectric films, formed by sol-gel and sputter deposition, were developed and analyzed for application as high speed nonvolatile memories. Ferroelectric liquid crystal devices were studied for application as fast electro-optic light valves in spatial light modulator applications. A novel thermo optical effect in ferroelectric lead magnesium niobate suitable for use in pressure sensing applications was discovered.			
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Project Summary

SUMMARY OF FINAL REPORT under ARO Contract DAAL03-90-G-0002 for the period 12/89 through 12/92 including **PROGRESS REPORT** for the period 7/1/92 through 12/31/92.

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Title of Project: Structure and Switching Dynamics in Ferroelectric Crystal and Liquid Crystal Thin Films
Army Research Office, Physics Program

Summary: The structure and switching dynamics of ferroelectric solid state and liquid crystal thin films were investigated experimentally using x-ray scattering, dielectric measurements, and optical microspectroscopy. Crystalline piezoelectric ferroelectric films, formed by sol-gel and sputter deposition, were developed and analyzed for application as high speed nonvolatile memories. Ferroelectric liquid crystal devices were studied for application as fast electro-optic light valves in spatial light modulator applications. A novel thermo optical effect in ferroelectric lead magnesium niobate suitable for use in pressure sensing applications was discovered.

The research direction of this program has been to advance the basic physical understanding of ferroelectric liquid crystal and crystalline ferroelectric thin film materials, a necessary step if the significant potential of their technological application 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 rate limits the commercialization of these technologies.

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 (submicrosecond) electro-optic response, a large electro-optic effect (rotation of a birefringent plate of $\Delta n \sim 0.2$ through an angle of 45°) 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.

Crystalline Ferroelectric Thin Film (CFTF) Devices

Thin films of solid state ferroelectric materials deposited on solid substrates are now recognized as the principal new technology for charge storage in Dynamic Random Access Memories (DRAMs) and for commercially practical nonvolatile RAMs. In addition CFTF nonvolatile memories exhibit the important advantage of radiation hardness. We propose too extend the application of CFTFs to optically addressed ferroelectric RAMs.

WORK CARRIED OUT

Project Areas

- Optical microscopy and x-ray scattering study of Ferroelectric Liquid Crystals (FLCs);
- Theoretical modelling of optical, flow, and transport effects in Surface Stabilized FLC (SSFLC) cells;
- Laser study of thermo-optical instabilities in ferroelectric crystals;
- Characterization and development of Crystalline Ferroelectric Thin Films (CFTFs) for integrated electronic applications.

Highlights of Accomplishments

In this and the following Section we highlight and then detail the work carried out under the prior grant period, referring by P# to the list of **Publications Resulting from the Support of the Prior ARO Grant** given below.

FERROELECTRIC LIQUID CRYSTALS

- Discovery of an optical symmetry of SSFLCs, confirming our model of the SSFLC layer structure [P9];
- Demonstration of the importance of polarization charge self interaction in SSFLC devices [P2];
- Discovery of the orientational plasticity of the FLC - rubbed polymer interface [P13, P22];
- Observation of the effects of thermal fluctuations on SSFLC switching dynamics [P11];
- Development and testing of a realistic model of ionic dopant effects in SSFLCs [P14];
- Elucidation of the director structure of SSFLCs via microscopy and transmission spectroscopy [P1, P6, P7, P12, P16, P24];
- Elucidation of the layer structure of SSFLCs via microscopy and x-ray diffraction for a variety of surface treatments [P1, P4, P10, P15, P21, P23, P26, P27, P29];
- Discovery of the surface electroclinic effect in the chiral smectic A phase [P8];
- Theoretical and experimental study of thermal surface orientational modes in a nematic liquid crystal, showing that surface modes require coupling to flow [P25, P28];
- Theory showing that backflow effects strongly influence the dynamics of switching in SSFLCs [P32];
- Demonstration of a "proximity effect" scrolling spatial light modulator [P5];

FERROELECTRIC CRYSTALS, THIN FILMS AND MEMORIES:

- Discovery of giant thermal-lens anomalies near crystal ferroelectric Curie temperatures [P34, P44];
- Discovery of optical bistability in ferroelectric films near their Curie temperatures [P47];
- Fabrication of ultra-sensitive flow-rate and pressure (1 milliTorr) gauges with no moving parts, using the optical bistability in PMN ceramics [P49];
- Discovery of period-doubling bifurcations en route to chaos in PMN bistable devices [P50];
- Characterization of DC leakage currents in PZT films -- $I(V)$ voltage dependence, $I(d)$ thickness dependence, $I(T)$ temperature dependence [P41, P38, P45];
- First successful integration of ferroelectric films into GaAs technology (as capacitors in 2.2 GHz receiver) [P46];
- Demonstration of depinning of ferroelectric domain walls in thin-film memories [P32];
- Development and characterization of very-low leakage current ferroelectric films for DRAMs [P43];
- Development of crack-free PZT patterned memories [P42];
- Discovery of Pt hillock formation on ferroelectric memory electrodes and demonstration that the hillocks were associated with Ti-rich Pt from the Ti-Si adhesion layer [P42];
- Demonstration of 5 MRad radiation-hardness of PZT memories [P39, P33];

Detail of Work under the Prior Grant

SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTALS

X-Ray and Microscopy Studies of Layer Structure of Ferroelectric Liquid Crystal Cells [P1, P4, P10, P15, P21, P23, P26, P27, P29]

The program of basic physics supported by this Grant has had a major influence on the understanding and development of electro-optic applications of Ferroelectric Liquid Crystals (FLCs). In earlier work we showed that the smectic layers in micron thick Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) films between solid flat plates could be chevron shaped¹ and that knowledge of the layer structure was essential for a quantitative understanding of SSFLC electro-optical properties.² Since that time we have pursued a program of x-ray scattering experiments to probe the SSFLC layer structure under a variety of conditions, including studying the effects of alignment layer and applied field. Following our finding the chevron structure, there were several published electro-optical studies of SSFLCs^{3,4,5} from which the authors concluded that applied voltage reversibly uprighted the smectic layers from the chevron structure to the planar structure at voltages typically used to reorient the director in SSFLC devices. To test this we carried out the x-ray scattering experiments reported in P23, which showed that there is, in fact, virtually no layer alteration at switching voltages. This was in accord with our optical microscopy results and with elastic modelling of the system. Our optical modelling was able to account for the above optical observations with fixed chevron-shaped layers. We have produced a model for the structure which mediates the change in chevron interface position, which we have named the "mountain" defect because of its appearance P29. This is an important subclass of chevron related defects in SSFLC cells. At higher voltages there is irreversible layer reorientation in the form of characteristic line "roof-top" defects, the structure of which we have studied via x-rays P26. The scattering provides us with a probability distribution of layer orientations which has enabled us to model the layer structure of these defects. We have determined the layer structures obtained with high pretilt parallel (chevron) and antiparallel (tilted layer) alignment treatments P4 as well as the layer structure (tilted planar) obtained when the ferroelectric smectic phase is entered directly from the nematic P10. The x-ray scattering results and their implications for SSFLC switching and defects have been published in invited reviews P1, P21.

We have studied via optical microscopy, the generation of the so-called "stripe texture" obtained in some SSFLC cells^{6,7,8} reversibly at zero or low fields and irreversibly at high fields. We were able to show that the stripes are adjacent zig-zag defects^{P21} at low field and model the process which produces a permanent folded layer geometry at high field P15. We studied the switching characteristics of cells having adjacent stripe and chevron layer texture, and found them to be very similar, indicating that the surfaces are the operative stabilizing interaction in stripe cells, not the stripes, as has been claimed.

Director Distribution and Dynamics in SSFLC Cells [P1, P2, P6, P7, P9, P12, P24]

We have continued our studies of the dynamic of director reorientation in response to applied field in SSFLCs, showing that polarization space charge interactions P2 lead to the formation of soliton-like structures^{9,10} in the SSFLC geometry¹¹, in which the director becomes uniform throughout most of the cell. These polarization space charge effects are of relevance in essentially any practical SSFLC device. A basic unsolved problem in the physics of SSFLC cells is the origin of the shape of the domains mediating the switching of chevron SSFLC cells. These domain boundaries, which are essentially surface disclinations trapped at the chevron interface, adopt a remarkable faceted "speedboat" shape which appears to be dynamically stabilized. Thus the velocity vs. domain boundary orientation is modulated by low velocity cusps, with relative facet velocities ranging over an order of magnitude at low fields. We have completed in P24 a stroboscopic visualization of these domains, characterizing their nucleation and growth behavior vs. applied field and temperature. These results will serve as a guide for the future modelling of this process.

We have completed our microspectroscopy of the light transmitted by SSFLCs P6, P7, P12 showing that we can describe quantitatively the characteristics of the inhomogeneous anisotropic SSFLC dielectric medium. In this study we discovered a fundamental optical symmetry of SSFLCs P9, a result of the time reversal symmetry of light passing through a nonabsorbing SSFLC cell and the reflection of the chevron interface position through the cell midplane as a zig-zag wall is crossed P1. This observation provides convincing evidence for the chevron-based model of SSFLC layer-director structure which we proposed P1.

Yoshino has reported a very interesting light scattering effect in thick (50 - 100 μm) FLC cells in which they become highly scattering during transient field reversal¹². We have demonstrated in P11 that thermal fluctuations can play a significant role in this process. Under conditions of field reversal, the ferroelectric polarization P is initially oriented by a strong field, eE , which is then rapidly changed in sign. Then on the average $P \sim e$, but in metastable orientational equilibrium (average torque is zero). However, thermal fluctuations will locally rotate P away from e , in opposite orientational directions in different places, and this motion will be continued by the field to produce a domain wall foam which scatters light. Eventually holes open up in the walls and as it coarsens the scattering decays away. This result shows the importance of including thermal fluctuations into the dynamical description of FLC director reorientation.

Director Distributions and Surface States in Hexatic (smectic I) SSFLC Cells [P16];

There has been one attempt to understand the switching of chiral smectic I liquid crystals in the SSFLC geometry¹³ in which up to eight distinct orientation states can be found (some field stabilized, see Figure 4). With an understanding of the chevron structure in hand our optical microscope studies have enabled us to work out for the first time the correct director distributions and interfacial smectic I orientations. We find eight distinct orientation states, indicating that the rows of molecules corresponding to the 10 miller indices of the hexatic lattice are parallel to the walls and to the chevron interface and that there are four stable (three field stabilized) orientations of the director at the solid interfaces and two at the chevron interface. This is the first experiment exhibiting the orientation of a hexatic lattice by a surface.

Ion Transport and Backflow Effects [P14, P32]

We have developed our computer modelling of SSFLC cells to the point where realistic treatment of more complex effects can be modelled. We have extended our previous simulations to include the additional effects of either ion doping P14 or the coupling of flow P31 to director reorientation. A simple model of ion drift

shows that the ion current pulse occurs when the ions have reached only halfway across the cell, in contrast to earlier models. Our flow simulations P31 have been particularly exciting, showing two principal effects: (1) *Molecular reorientation accompanying electro-optic switching sets up transient flow of the liquid crystal which, in turn, modifies the reorientation.* Enhancements in switching speed of ~ 5 result, as shown in Figure 1. Here we present the polarization orientation $\phi(z,t)$ in an SSFLC cell vs. the position between the plates, z , and time, t , both with and without flow coupling, following a reversal of applied electric field. Without flow coupling a reorientation soliton travels across the cell to affect switching. With flow coupling the flow set up by the starting soliton begins to reorient the polarization throughout the cell and it switches uniformly when the soliton is only a quarter of the way across; (2) *The reorientation induced flow acts as a pump, producing a net displacement of the FLC along the smectic layer direction.*

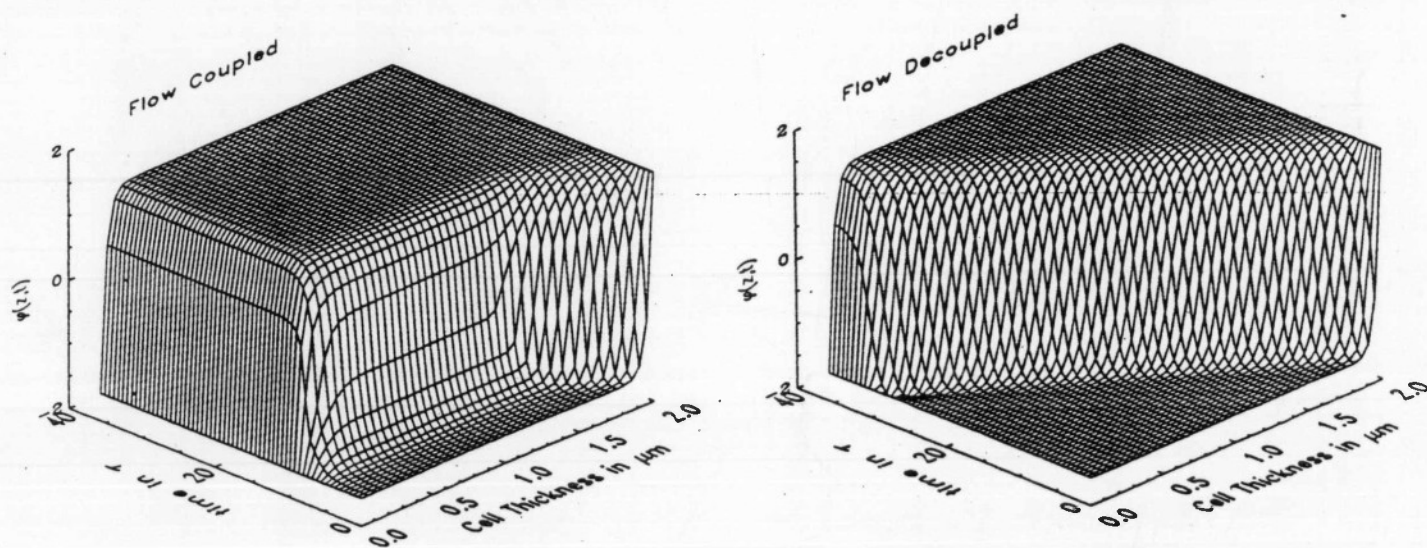


Figure 1: The polarization orientation $\phi(z,t)$ in an SSFLC cell vs. the position between the plates, z , and time, t , both with and without flow coupling, following a reversal of applied electric field. Without flow coupling a reorientation soliton travels across the cell to affect switching. With flow coupling the flow set up by the starting soliton begins to reorient the polarization throughout the cell and it switches uniformly when the soliton is only a quarter of the way across. Thus the flow coupled response time is $\sim 1/4$ of the flow uncoupled.

Surface Orientation States, and Orientational Plasticity at an FLC -Rubbed Polymer Interface [P13, P22]

We have extended our previous Total Internal Reflection (TIR) studies of director orientation at the FLC-glass interface¹⁴ to begin to look at cases where the solid surface is an aligning layer such as rubbed polymer or oblique SiO. The rubbed polymer (nylon 6/6) case proves to be particularly interesting. The depolarized reflectivity $R(\beta)$ from the FLC-glass interface vs. sample orientation β about the normal to the glass surface, for light propagating in the glass and evanescent in the liquid crystal. $R(\beta)$ has a minimum at $\beta = 0$, indicating

molecular orientation along the rubbing direction in both the smectic A and smectic C phases. Interestingly the director does not reorient on the surface upon going well below the A-C transition temperature, even though the smectic A surface orientation is not compatible with the adjoining smectic C structure. Applying an electric field however produces the expected smectic C orientations and varying the electric field gives a hysteresis loop for switching between them, which shows that the surface has now irreversibly forgotten about the initial smectic A orientation and rubbing direction, behaving similarly to clean glass. This shows that the rubbed polymer-FLC interface behaves in an orientationally plastic way in the presence of the large field induced torque on the director obtainable in FLCs, but that before the field is applied the surface anchoring is strong enough to somehow overcome the bulk preference. The temperature of the hysteresis shows the presence of the ferroelectric polar surface interaction P13.

Surface Electroclinic Effect [P8]

Our TIR technique has also been applied to the smectic A phase, where we find at the surface an induced director tilt relative to the layer normal. We attribute this tilt to a surface electroclinic effect wherein the intrinsic polarity of the surface expresses itself by inducing a ferroelectric polarization and therefore director tilt at the surface.

Proximity Effects in SSFLCs [P5]

We have studied the behaviour of pixellated SSFLC cells with ultrasmall ($\sim 5 \mu\text{m}$) gaps between pixels. With this geometry the switching threshold for a given pixel will depend of the SSFLC state of its neighboring pixels, i.e. there will be a proximity effect. If this is the case then a scrolling spatial light modulator can be constructed, in which data is fed into a row of pixels at one end and shifted (scrolled) down the row by a periodic signal having the appropriate relative phase shift between pixels. We demonstrated the basic proximity effect.

Director Fluctuations at the Nematic-Solid Interface [P25, P28]

Our TIR probe of director orientation at the FLC-solid interface, discussed above, suggested the possibility of studying the dynamics of interfacial director orientation fluctuations using Quasielastic Light Scattering Spectroscopy. To pursue this we began with an experiment on a nematic-solid interface since this is a simpler situation than the FLC case, using 5CB, a well-studied nematic whose elastic constants and viscosities are known. The experiment showed that it was possible to collect QELS correlation functions from director fluctuations illuminated at the surface by an evanescent wave in the nematic. In collaboration with Martin Copic, a visiting researcher in our laboratory from the J. Stefan Institute in Ljubljana, we have started to analyze this scattering theoretically and have obtained some interesting results. Our first effort was a model having the director orientation field as the only field variable, including its elasticity, orientational viscosities and surface interaction. Interestingly this model produces no surface mode, the scattering coming from a superposition of the tails of the bulk modes at the surface P25. However, upon allowing the liquid crystal to flow and considering the coupled velocity-orientation fields, a distinct surface mode is obtained for certain of the geometries and parameter values P28.

FERROELECTRIC CRYSTALS, THIN FILMS AND MEMORIES

The Thermo-Optical Lens Effect in Ferroelectric Crystals and Flow-Rate Gauges based on Thermal Focusing [P34, P44, P47, P49, P50]

The thermal focusing and optical bistability we discovered in PMN (lead magnesium niobate) can be used to fabricate small, robust sensors. The sensors are very sensitive to air pressure; in fact, they are unique pressure sensors in that they have no moving parts. Instead they react to subtle changes in convective heat loss at the PMN surfaces. These sensors can also be used as flow-rate meters, since the convective heat loss at the surface is also sensitive to air flow. We have shown P49 that these sensors can measure pressures to 10 millitorr (absolute) and flow rates as low as 0.3 m/s in air. We have received a formal letter of request from William Lawless, President of CeramPhysics, Inc., in Westerville, Ohio to market this device to gas

pipeline companies in the USA. This is another example of technology transfer to US industries of the R&D results from our ARO grant.

In what follows we outline our current understanding of the physics of these devices:

These PMN thermal lenses transmit two stable light patterns through them; call them pattern A and pattern B. The time dependence of a particular spatial light pattern transmitted is given by

$$I(t) = I(0) [1 - 0.58 b(1 + t_c)^{-1}], \quad (1.)$$

where the relaxation time t_c is a function of external parameters such as temperature T .

In addition, t_c is a function of prior history; in particular, it depends upon the number of times N the thermal lens has already oscillated:

$$t_c(N) = t_{c0} e^{0.72N}, \quad (2.)$$

which is an empirical experimental law that does, however, satisfy the May-Leonard nonlinear predator-prey equations, which have been used earlier by D.Z. Anderson¹⁵ to describe mode competition in phase conjugate optics experiments.

The dependence of $t_c(N)$ upon laser power is inverse (hyperbolic), satisfying

$$t_c(N) = A/(P - P_N), \quad (3.)$$

where P_N is the laser power threshold for the N th switching event.

For convection calculations in quiescent air we can neglect the radiation loss term at the surface and estimate the net heat flow from the surface due to convection as

$$H = k_{air} N_n / dd, \quad (4.)$$

where k is the thermal conductivity of air, N_n , the Nusselt number (which we estimate as 23); and d , the PMN specimen diameter. This equation predicts a temperature drop ΔT of 1.0K at the PMN sample under normal conditions of operation in which it is used as a pressure sensor.

For non-quiescent conditions in which the sensor is used to measure flow rate, the heat loss due to convection is given by

$$H = P/(A \Delta T), \quad (5.)$$

where A is the specimen surface area (neglecting the ends of the rod). H is still given by Eq.(4) in this case, also, but the Nusselt number for non-quiescent conditions must be calculated from the Rayleigh number R corresponding to the flow rate V and geometry employed:

$$R = Vd/\nu, \quad (6.)$$

where ν is the kinematic viscosity of air ($15.89 \mu m^2/s$ at 300K);

$$N_n = C K^m P_r^n, \quad (7.)$$

where P_r is the Prandtl number, C , the friction coefficient; $m = 0.60$; and $n = 0.37$. This gives Nusselt numbers from 8 to 40 for the flow rates we used.

For a flow rate of 33 M/s (the maximum we employed), this predicts a temperature discontinuity at the PMN surface of 18K. We can test this model by comparing our optical bistability data at different flow rates and temperatures. When this is done, we find that a flow rate of 33 m/s corresponds to a temperature change of 23K. Thus, the two techniques give ΔT of 18 and 23K in each case.

It is also useful to examine the self consistency of the thermal conductivity K of the PMN evaluated via two different techniques: If we neglect lens aberrations, then the relaxation time t_c of the thermal lens pattern is given by

$$t_c = w^2 \rho C_p / (4K), \quad (8.)$$

where w is laser beam waist; ρ , density; and C_p , specific heat. We can compare this value of K with that obtained from the angular beam divergence angle ϕ :

$$K = 0.12P (\pi w n \phi)^{-1} (dn/dT) (1 - I_{trans}/I_o), \quad (9.)$$

where n is the index of refraction; I_{trans}/I_o , the percentage of laser-beam intensity not absorbed or reflected. The two calculation in Eqs. (8,9) agree within a factor of two and give $K(\text{PMN}) = (2.4 \pm 0.8) \times 10^{-4} \text{ cal}/(\text{cm s K})$.

These studies permit a dynamic "phase diagram" to be constructed that plots flow-rate and/or pressure versus laser input power (and hence ΔT at the sample-air interface). The phase boundary that separates the c.w. oscillation regime from that of a discrete number of pulses is found to be described by:

$$\Delta T = Pd/AN_n k_{air} - MV^{0.30}, \quad (10.)$$

where $M = 6.5 \text{ m}^{-0.3} \text{ s}^{0.3}$, and the other parameters have been defined in preceding equations.

While aspects of this basic picture has been confirmed, there are a variety of questions which remain unanswered, concerning principally the nature of the operative nonlinearity and its instabilities and concerning the qualitative characteristics of the system in various regions of the large parameter space available.

Publications Resulting from the Support of the Prior Grant

FERROELECTRIC LIQUID CRYSTALS

- P1. "DIRECTOR AND LAYER STRUCTURE OF SSFLC CELLS," N.A. Clark, T.P. Rieker, and J.E. MacLennan, *Ferroelectrics* 85, 79-97 (1988).
- P2. "DEVICE APPLICATIONS OF FERROELECTRIC LIQUID CRYSTALS: IMPORTANCE OF POLARIZATION CHARGE INTERACTIONS," Z. Zhuang, J.E. MacLennan, and N.A. Clark, *Proceedings of the Society of Photo-optical Instrumentation Engineers* 1080, 110-114 (1989).
- P3. "NOVEL LIQUID-CRYSTAL PHASE-TRANSITION BEHAVIOR AT THE CHIRAL NEMATIC-SMECTIC A-SMECTIC-C POINT," D.S. Parmar, N.A. Clark, D.M. Walba, and M.D. Wand, *Physical Review Letters* 62, 2136-2139 (1989).
- P4. "LAYER AND DIRECTOR STRUCTURE IN SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTAL CELLS WITH NON-PLANAR BOUNDARY CONDITIONS," T.P. Rieker, N.A. Clark, G.S. Smith, and C.R. Safinya, *Liquid Crystals* 6, 565-576 (1989).
- P5. "PROXIMITY EFFECT FOR SCROLLING SPATIAL LIGHT MODULATOR APPLICATIONS OF SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTAL (SSFLC) SWITCHING," R.E. Brooks, N.A. Clark, M.A. Handschy, T.P. Rieker, *Applied Physics Letters* 56, 1646-1648 (1990).
- P6. "DIRECTOR ORIENTATION IN CHEVRON SURFACE-STABILIZED FERROELECTRIC LIQUID CRYSTAL CELLS: VERIFICATION OF ORIENTATIONAL BINDING AT THE CHEVRON INTERFACE USING VISIBLE POLARIZED LIGHT TRANSMISSION SPECTROSCOPY," J.E. MacLennan, N.A. Clark, M.A. Handschy, and M.R. Meadows, *Liquid Crystals* 7, 753-785 (1990).

- P7. "DIRECTOR REORIENTATION DYNAMICS IN CHEVRON FERROELECTRIC LIQUID CRYSTAL CELLS," J.E. MacLennan, M.A. Handschy, and N.A. Clark, *Liquid Crystals* 7, 787-796 (1990).
- P8. "SURFACE ELECTROCLINIC EFFECT IN CHIRAL SMECTIC-A LIQUID CRYSTALS," J.-Z. Xue and N.A. Clark, *Physical Review Letters* 64, 307-310 (1990).
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- P10. "CHEVRON LAYER STRUCTURES IN SURFACE STABILIZED FERROELECTRIC LIQUID CRYSTAL (SSFLC) CELLS FILLED WITH A MATERIAL WHICH EXHIBITS THE CHIRAL NEMATIC TO SMECTIC C* PHASE TRANSITION," T.P. Rieker, N.A. Clark, and C.R. Safinya, *Ferroelectrics* 113, 245-256 (1991).
- P11. "THERMAL FLUCTUATION EFFECTS IN FERROELECTRIC LIQUID CRYSTAL POLARIZATION REVERSAL: LIGHT SCATTERING FROM A TRANSIENT DOMAIN WALL FOAM," J.E. MacLennan and N.A. Clark, *Physical Review A* 44, 2543-2557 (1991).
- P12. "VISIBLE POLARIZED LIGHT TRANSMISSION SPECTROSCOPY OF ELECTRO-OPTIC SWITCHING BEHAVIOR IN FERROELECTRIC LIQUID CRYSTAL CELLS," Z. Zhuang, N.A. Clark, J.E. MacLennan, *Liquid Crystals* 10, 409-417 (1991).
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- 6. Subha Mangalampalli. "BRILLOUIN SCATTERING STUDY OF SWOLLEN LYOTROPIC LAMELLAR LIQUID CRYSTALS," University of Colorado (1992).
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FERROELECTRIC LIQUID CRYSTALS

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- 2. "SURFACE-STABILIZED FERROELECTRIC LIQUID CRYSTALS," 13th International Liquid Crystal Conference, Vancouver, Canada (1990).
- 3. "THE STRUCTURE OF ELECTRIC-FIELD-INDUCED LAYER DEFECTS IN SURFACE-STABILIZED FERROELECTRIC LIQUID CRYSTAL DISPLAY CELLS," Meeting of Society for Information Display, International Symposium, Las Vegas, NV (1990).
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- 9. International Symposium Applied Ferroelectricity (ISAF), Urbana, IL, June 1990.
- 10. US-Japan Binational Conference on Electronic Ceramics, Kyoto, Dec. 1990.

11. Japan Electronics Industry Association annual meeting, Tokyo, Dec. 1990.
12. Conference on Fundamental Properties of Ferroelectrics, Williamsburg, VA, Feb. 1991.
13. Materials Research Society, Anaheim, CA, April 1991.
14. Combined IEEE/TMS Conference, Boulder, CO, June 1991.
15. Materials Research Society, Boston, MA, Dec. 1991.
16. TMS (Metallurgy) Conference, Boulder, CO, June 1991.
17. ISIF (Integrated Ferroelectrics), Monterey, CA, March 1992.
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20. International Conference on Domain Walls, Nantes, France, July, 1992.
21. ISAF, South Carolina, August 1992.
22. International Congress Vacuum Society, The Hague, Holland, Oct., 1992.
23. National Conference American Vacuum Society, Chicago, Nov. 11, 1992.
24. IEEE, San Diego, Dec. 1992.
25. Materials Research Society, Boston, Dec. 1992.

TECHNOLOGY TRANSFER

While the major focus of our work carried out under the previous contract period and that proposed to be done is the basic physics of CFTF and SSFLC devices, our overall scientific program places considerable emphasis on technology transfer and on the use of knowledge gained to support the development of applications. This aspect of our activity involves the following:

Crystalline Ferroelectric Thin Films

The principal area of technology transfer 1989-92 from our group at the University of Colorado in the area of crystalline ferroelectric thin films has been in integration of high-dielectric films into Si or GaAs memory devices. Most of our technology transfer is handled through a CU spin-off, Symetrix Corporation. The University of Colorado was given approximately \$250,000 by Symetrix in exchange for intellectual property relating to this thin-film technology. In addition, Symetrix pays salaries for about six CU graduate students and hires several CU faculty as consultants. We think that this is an outstanding example of technology transfer from university laboratory to small spin-off companies and finally to large international corporations.

The following is a list of the principal industrial participants and the status of each use:

1. General Motors (Delco Division). We have contract negotiations under way with GMR to coat their substrates with barium strontium titanate thin films for high-frequency capacitors.
2. Philips Corp. (Eindhoven, Holland). Sale of \$20,000 worth of PZT (lead zirconate-titanate) sol-gel.
3. McDonnell-Douglas Corp. (Huntington Beach, CA). Sale of \$20,000 worth of PZT sol-gel. Limited consulting.
4. Micron Technology (Boise, Idaho). We have contracts nearly completed to license technology to Micron for production of high-dielectric DRAMs.

5. Harris Semiconductor Corp. (Melbourne, FL). We delivered processing technology and materials to Harris for two years in the area of PZT films. Approximate value: \$200,000.
6. Matsushita Electronics Corp. (MEC). We have received approximately \$900,000 from MEC to license technology involved in ferroelectric films integrated into GaAs MESFET MMICs. This was the first successful (world-wide) integration of ferroelectrics into GaAs technology. A 2.2 GHz tuner is in commercial production (300,000/month) with royalties; a ferroelectric microprocessor (top-end, low-noise) is in limited prototype production and has been successfully tested.
7. Olympus Optical Corp. We have produced a 1 kb nonvolatile RAM with a new (secret) material that exhibits no fatigue or aging.
8. We have three other technology transfers underway: a) Licensing of our thin-film technology to the leading (Canadian) producer of hearing aids. (They need capacitors whose higher dielectric constant permits smaller sizes.) b) Licensing technology to a San Jose corporation that needs dielectric capacitors to be deposited on aluminum (this entails low-temperature processing.) c) Licensing the liquid-source CVD machine we invented to a Japanese manufacturer.

The University of Colorado has become a center where M.S. and Ph.D. students are being produced with expertise in ferroelectric memories and related devices; this will fill a perceived short-term need for staffing government and industrial laboratories.

At present the fundamental, non-proprietary studies of these memories is carried out in our University laboratories with ARO support and published in the open literature and in student theses. The proprietary aspects such as deposition techniques and exact formulations of sol-gel precursors (we use a xylene solution) are carried out by Symetrix Corporation, in cooperation with DOD laboratories. Some of the fabrication of parts by Symetrix is subcontracted to the University Microelectronics Laboratory. This has produced a good working symbiosis, which is enlarging to become a consortium involving DOD in-house labs.

Surface Stabilized Ferroelectric Liquid Crystals:

We have formed Displaytech, Inc. in Boulder, CO, a University spin-off development company working exclusively on FLC technology. Professor Clark is Chairman of the Board of Displaytech. Displaytech currently has thirty employees carrying out contract applications development, product development, manufacturing, materials synthesis and development, and marketing. From 1989 to 1992 over \$3,000,000 of contract research and development was carried out at Displaytech for both federal agencies and private companies, directed toward commercialization of FLC technology. Currently there are thirty five SBIR contracts completed or under way. Displaytech is currently the only company in the world with FLC products on the market. These include shutters, beam switches, and various linear and matrix light valve arrays. Displaytech has recently introduced VLSI-SSFLC active matrix addressed spatial light modulators, brochures.

We are actively licensing our SSFLC patents, generating royalty income to the University of Colorado of about \$40,000 in 1992. Canon, Inc., one of our licensees, is constructing a manufacturing plant, to be completed in 1993, which will have a capacity of 5,000 21" diagonal SSFLC workstation screens per month. These displays, now in production on a prototype fabrication line, are truly impressive: 1280 x 1100 16 color pixels in a 21" diagonal screen, 20:1 contrast, 25 Hz frame rate, flicker free, and 1" thick with its backlight. The potential of SSFLC displays is significant enough for the SI to have selected SSFLC co-inventors Noel Clark and Sven Lagerwall and FLC inventor Robert Meyer for their Special Recognition Award in 1989.

In 1991 we organized the Third International Ferroelectric Liquid Conference on the University of Colorado campus, hosting some 200 FLC researchers from around the world. A variety of exciting new results in FLC materials, applications, and basic science were presented, highlighting the continued intense interest in FLCs. Conference Proceedings were published in two volumes of the journal *Ferroelectrics*.

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