CHINESE JOURNAL OF PHYSICS VOL. 33, NO. 3 JUNE 1995

Studies of Polymer-Stabilized Cholesteric Liquid Crystal Texture Films

Andy Y. G. Fuh, C.-Y. Huang, M.-S. Tsai, and G.-L. Lin
Department of Physics, National Cheng Kung University, Tainan, Taiwan 701, R.O.C.

S.-J. Chang
Department of Electrical Engineering, National Cheng Kung University, Tainan, Taiwan 701, R.O.C.

(Received February 22, 1995)

Cells of polymer-stabilized cholesteric texture (PSCT) were fabricated with various polymer concentrations. The structure of the polymer network and the electro-optical characteristics of the devices were studied. The result clearly demonstrates the polymer stabilization effect on the liquid crystal domains in the cells. In addition, the hysteresis characteristics and the dielectric properties of the cells were studied as a function of the driving frequency. The results lead to the conclusion that the polymer enhanced hysteresis effect in PSCT cells is mainly caused by the aligning effect of the polymer network.

PACS. 78.20. Jq – Electra-optical effects.

I. INTRODUCTION

Liquid crystal polymer dispersions have been studied intensively in recent years. These materials include standard polymer-dispersed liquid crystals (PDLC's) where the concentration of polymer in the mixture is usually more than 20% in order to confine LC's. In addition to being used as displays and variable transmittance windows [1-13], PDLC films have also been reported for uses as a gaussian filter [14] and switchable grating [15]. The other type is liquid-crystal-dispersed polymers which the polymer concentration is usually low (1-5%) for use to stabilize the LC structure in the cell, so called the polymer-stabilized textures. The liquid crystals used in this technology are cholesterics [16]. Polymer-stabilized cholesteric texture (PSCT) films have been reported to show high promise for display applications.

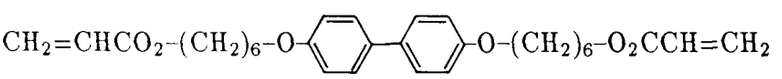
Depending on the treatment on the substrates and on the pitch length p of the employed cholesteric liquid crystal, three types of display devices can be formed. Based on

the mode of operation, they are classified into normal-mode (opaque in a field-off condition and clear in a field-on condition), reverse-mode (clear in a field-off condition and opaque in a field-on condition) and color-reflective bistable cells [16-18]. Because the concentration of the polymer in these cells is so small that the refractive-index matching condition between the polymer and liquid crystal as required in PDLC films is no longer need. Therefore, PSCT cells are haze-free for all wide viewing angles.

In this paper, we report the results obtained from the studies of the hysteresis characteristics in the transmittance versus applied voltage curves of the PSCT cells operating in the normal-mode under various conditions. It was found that the hysteresis effect due to the cholesteric-nematic phase transition [19] was enhanced and stabilized by dispersing a small amount of polymer in the liquid crystal. The aligning effect of the polymer network is no doubt one of the factors that give rise to this hysteresis enhancement. The other source could be the space charges trapped by the polymer network since they could distort the electric field in the cell. To verify whether the polymer enhanced hysteresis effect is associated with the trapping charges. We, further, measured the cell's hysteresis and dielectric characteristics as a function of the driving frequency. The results show that the hysteresis width is kept constant in the frequency range where the cell transits from being as a resistor to a capacitor. It indicates the polymer enhanced hysteresis effect in PSCT cells is mainly due to the aligning effect of the polymer network.

II. EXPERIMENTALS

The liquid crystal used in this experiment is a mixture of a nematic E48 and a chiral compound CB15 (both are from E. Merck). The pitch length p of this cholesteric LC was adjusted to be $\sim$ 1.5 μm by adding $\sim$ 8wt% chiral compound in the mixture. It means this cholesteric film aligned in the planar texture reflects light of wavelength $\lambda \sim$ 2.25 μm determined by the Bragg formula $\lambda = np$, where n is the average refractive index of the liquid crystal [20]. A small amount of monomer was then added to the resulting cholesteric LC. The monomer has the chemical structure



As seen, it has a rigid core and two flexible hydrocarbon tails. At the end of the hydrocarbon tail there is a reactive double bond which can be polymerized to form cross-linked polymer network under UV irradiation. In this experiment, the concentrations of the monomer added into the mixtures were O-3.3 wt%. To initiate the polymerization, a small of photoinitiator, benzoin-methy-ether (BME) ($\sim$ 10 wt% of the monomer) was added to the mixtures.

15 μm of glass spheres were then added to the LC/monomer mixtures to control the film's thickness. The mixture was finally sandwiched between two indium-tin-oxide (ITO) coated glass slides to form a sample. Our normal-mode PSCT cells were fabricated following the same way reported by Yang et al. [16] Briefly, cells were made without any surface treatment on the glass substrates; the filled cell was polymerized using UV light with the LC molecules aligned in the homeotropical texture with the application of a 1 KHz square-wave voltage having $V_{rms} \sim 40$ V for $\sim$ 30 minutes. The UV light was provided by a Philips model 400/30s metal halide lamp. It was operated to give the total UV intensity in the wavelengths 350-400 nm$\sim$ 200 mW/cm^2. Two samples were made for each mixture; one was for the measurements of the device's electro-optical characteristics, the other was for the study of the polymer network formed in the cell after curing. The polymerization took place at room temperature.

The experimental setup for measuring the devices' electro-optical (E-O) characteristics was given in Ref. [12]. But the sample was mounted in a thermal chamber in the present case. The amplitude of the applied square-wave voltage V_{rms} (1 KHz) increases initially from 0 V to the saturated voltage $\sim$ 40 V and then decreases back to zero in a step of 0.25 V/sec.

For the polymer network study, the cells were put in haxane solvent to remove the liquid crystal. After the liquid crystal was dissolved in the solvent, we split the cell. Special attention was paid not to disturb the structure of the polymer network in the splitting. Although the removal of the liquid crystal was slow and took a few days, hexane was effective in removing the liquid crystal without deforming the polymer network. The solvent with dissolved liquid crystal was allowed to evaporate in a vacuum chamber. The network was coated a thin film of Palladium ($\sim$ 40 nm thick) and investigated by SEM (Scanning Electron Microscope).

The dielectric properties of the cell having $\sim$ 2.1 wt% of monomer were then measured as a function of the frequency of a constant sinusoidal voltage, 1 Hz to 10^6 Hz, using a Schlumberger Instruments model SI 1260 Impedance Analyzer. Finally, the same cell's E-O characteristics were measured as a function of the driving frequency. The relation of AV versus frequency was then deduced from these measurements.

III. RESULTS AND DISCUSSIONS

Figure **1** shows the edge-view SEM image of the polymer network for the cell filled with the mixture having $\sim$ 2.1 wt% monomer. It can be seen that the polymer network

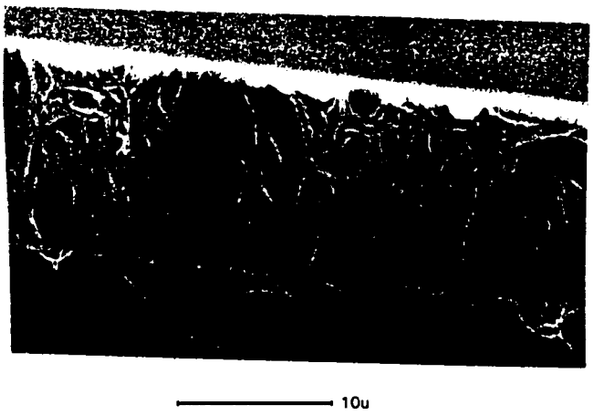


FIG. 1. The edge-view SEM image of the liquid crystal free polymer network in a PSCT cell having ~2.1 wt% monomer.

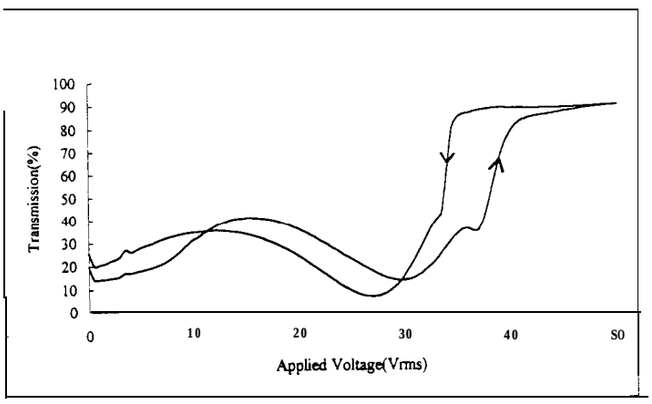
is anisotropic and perpendicular to the glass surface. It has been reported that polymer network structure formed in a liquid crystal environment can be controlled by the configuration of the liquid crystal during curing [21]. In the present case, the liquid crystals in the cell were oriented in the homeotropical texture during the polymerization of the monomer. Thus the structure shown in Fig. 1 having the network perpendicular to the glass surface is reasonable. It should be emphasized that, after polymerization, the polymer network in turn affects the orientation of the liquid crystals. Since the network, in the present case, is perpendicular to the glass surface, it tends to align the LC's around it to be in the same direction, i.e. the homeotropical alignment. This is the so called aligning effect.

Once the polymerization is completed and the field is removed, the orientation of the liquid crystals is determined by the two competing forces; the twisted distortion force of the intrinsic nature of the cholesteric liquid crystal and the aligning effect of the polymer network. It is found, in the present case, that the LC's in the cells having monomer concentrations less than ~ 4.5 wt% will relax back to helical structure and settle in domains. These domain formations are also called focal-conic textures. The function of the polymer network is to limit the growth of these domains and also to stabilize them. In other words, the LC's will be maintained in the homeotropical texture, due to the polymer aligning effect, permanently after polymerization, if the monomer concentration is higher than 4.5 wt%. This critical monomer amount is found to be dependent on the pitch length of the cholesteric LC employed.

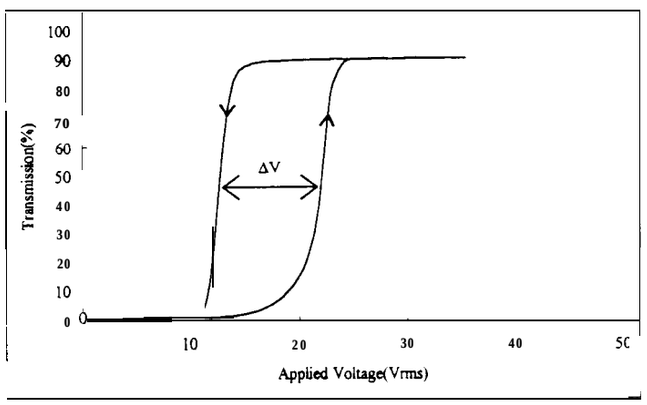
The variations of the size and the density of the polymer network with respect to the

monomer concentration were also measured. The result (not shown) shows that the size is not sensitive to the monomer concentration, but affected by the curing rate. However, the density is increasing with the monomer concentration.

Figure 2 shows the measured E-O characteristics of a cell filled solely with the cholesteric liquid crystal (Fig. 2(a)) and a PSCT cell having ~ 2.1 wt% monomer in the mixture (Fig. 2(b)). They both show similar features. At low applied voltages, the cells are in the focal conic texture and the transmittance is low, When the voltage is



(a)



(b)

FIG. 2. The measured electro-optical characteristics of (a) a cell filled with solely a cholesteric LC, (b) a PSCT cell having ~ 2.1 wt% monomer in the mixture.

increased above the threshold: they are switched into homeotropical texture and the transmittance is high [16]. Now we decrease the voltage, the films exhibit a pronounced hysteresis effect. It can be seen however that the PSCT cell shows a lower and stabler transmittance in the voltages below the threshold. This can be understood as follows. Since the cell made solely from cholesteric LC contains various domain sizes of the focal-conic textures. Some of them are too large to scatter light effectively. Therefore a great deal of light passes through the cell in this voltage range. Furthermore, the focal-conic domain sizes are not stable, and change with time rapidly, it gives rise to the fluctuation in transmittance. With an appropriate polymer network density, the domains with too large a size will be suppressed, and the smaller and the more uniform domains can be maintained; hence, the scattering effect is maximized and stable. In addition, it is noted the PSCT cell also exhibits a larger hysteresis width and a lower threshold voltage. These reductions are mainly due to the alignment effect of the polymer network.

In order to characterize the hysteresis effect, we define the hysteresis width AV as the difference between the voltages corresponding to the half maximum transmittance in the rising and falling curves as shown in Fig. 2(b).

The stabilization effect of the polymer network on LC domains in PSCT cells can also be seen clearly in their transient optical responses to a DC driving pulse. Fig. 3 shows the measured response curves for cells with 0, 1.1, 2.1 and 3.3 wt% monomer in the mixtures. A small echo peak is seen in the middle of the decay slope for the cell with no polymer

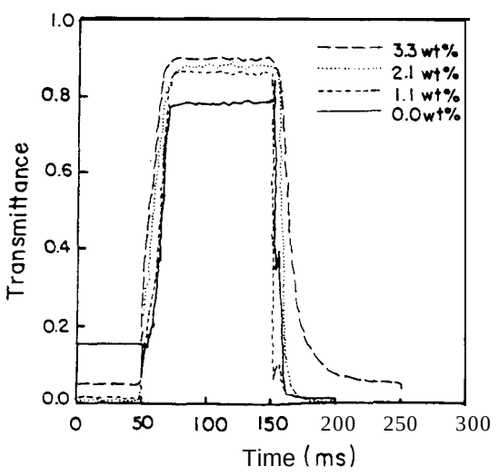


FIG. 3. **The** transient electro-optical responses of **PSCT** cells having 0, 1.1, 2.1 and **3.3** wt% monomer concentrations.

network. This is due to the optical bounce effect induced by the back flow during the relaxation of LC molecules when the field is removed [22]. It is shifted to a bit later for the cell having 1.1 wt% monomer, and eventually disappears in cells with 2.1 and 3.3 wt% monomer. Again, it is suppressed by the polymer network. From this Figure, the minimum amount of monomer needed in the mixtures, in order to stabilize the LC domains, can be estimated. It is $\sim$ 1.4% in the present case. Fig. 3 also shows a dip and a spike at the beginning and at the end of the driving pulse, respectively, for the cell having no monomer. They are caused by the transient changes in LC domain sizes at these moments. Finally another remark from Fig. 3 is made before closing this paragraph. It is seen the response times of the cells are affected by their monomer contents. It rises faster, but falls slower, if the cell has a higher monomer concentration. Again it is due to the aligning effect of the polymer net work.

Figure 4 shows the measured AV as a function of the dispersed polymer concentration x. AV is seen to keep $\sim$ 3 V for $x <$ 1.4 wt%. This hysteresis is basically arising from the cholesteric-nematic transition [19]. As the polymer's concentration is above 1.4 wt%, AV is increasing with the polymer concentration. The critical monomer amount required to stabilize the LC domains found in this part of experiment is consistent with that found in Fig. 3.

The hysteresis effect described above for PSCT cells is found to be similar to that of AC thin film electroluminescent (ACTFEL) devices based on $Y_2O_3/ZnS{:}Mn/Y_2O_3$ structure. Hysteresis ACTFEL devices have been reported to require a Mn-doping of at least $\sim$ 1 mol%, and the hysteresis width is also increasing with the dopant concentration [24].

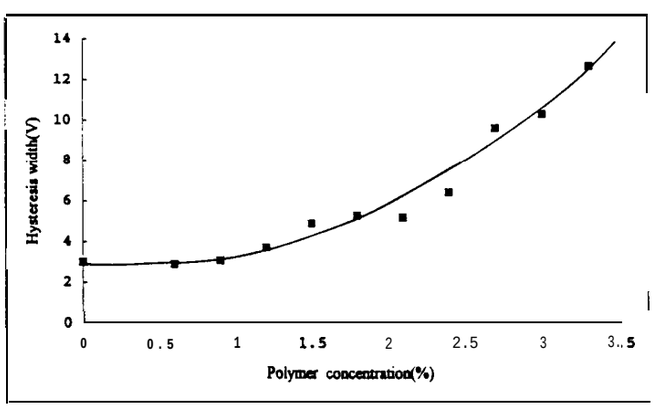


FIG. 4. The measured variations of the hysteresis width ΔV of a PSCT cell with respect to the monomer's concentration in the mixtures.

The mechanism leading to such a hysteresis behavior is not well understood as yet. But it is generally recognized to be due to the deeply trapped space charges which distort the electric field within the semiconductor layer [23].

In the present case, the PSCT material may be considered as a cholesteric LC doped with a small amount of monomer. The monomer is polymerized to form a cross-linked polymer network after curing. Under the application of a low-frequency AC voltage, the charged carriers could move. Some of them might be trapped by the polymer network and form space charges as those in ACTFEL devices.

To verify whether the polymer enhanced hysteresis effect in PSCT cells is associated with the trapping charge, we further measured both AV and dielectric characteristics as a function of the driving frequency. Electrically, a PSCT cell can be considered to be equivalent to being a resistor and a capacitor connected in parallel. Our dielectric study gives the cell's impedance and its phase angle as a function of the driving frequency. The measured results for the cell having $\sim$ 2.1 wt% monomer are shown in Fig. 5. It is seen that the cell transits from being as a resistor-like at f < 100 Hz to a pure capacitor at $\sim$ 1000 Hz. Therefore, if the trapping charges do exist, we should expect to see that the

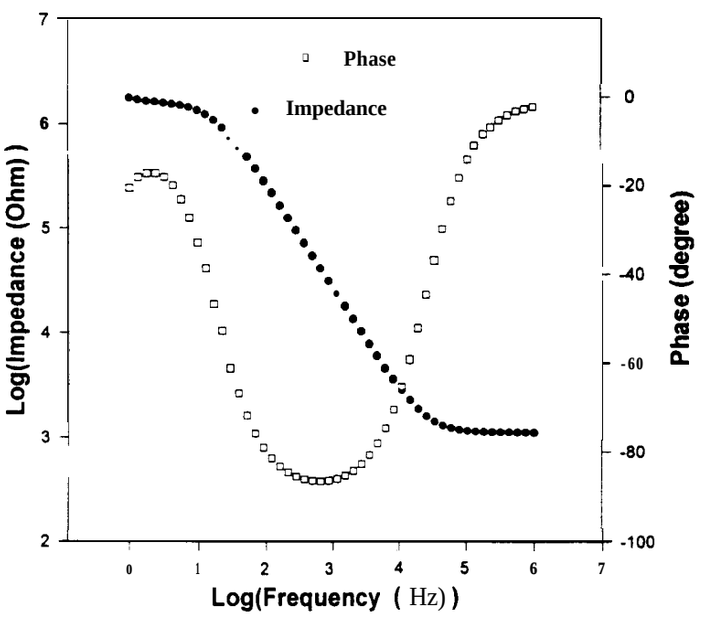


FIG. 5. The measured impedances and their phase angles of the cell having $\sim$ 2.1 wt% monomer as a function of the frequency of the driving voltage.

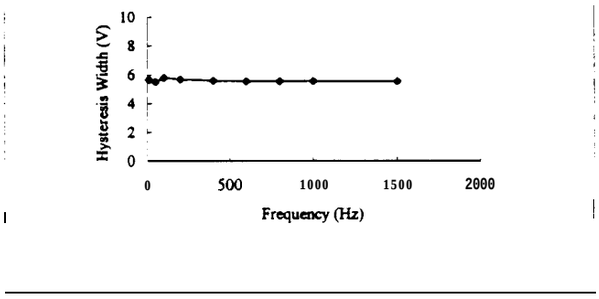


FIG. 6. The variations of the hysteresis width AV with respect to the driving frequency. The PSCT cell used had ~ 2.1 wt% monomer in the mixture.

cell's hysteresis width will be changed over this frequency range. The measured result of AV versus driving frequency shown in Fig. 6, however, shows AV is constant. Based on these results, we may conclude that the polymer enhanced hysteresis effect in PSCT cells is mainly due to the aligning effect of the polymer network.

Figure 7 shows the dependence of AV on the ambient temperature. AV is seen to decrease as the temperature is increasing. This is believed to be due to the weaker aligning force of the polymer network on the LC molecules at higher temperatures.

Finally it is noted the use of the pronounced hysteresis effect of a normal-mode PSCT cell to fabricate a projection-type matrix LCD is evident. The driving scheme is shown in Fig. 8. For simplicity, we have now 3 x 3 matrix LCD. Addressing the display is done one

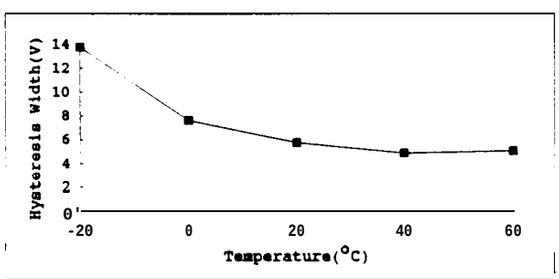


FIG. 7. The measured AV as a function of the ambient temperature

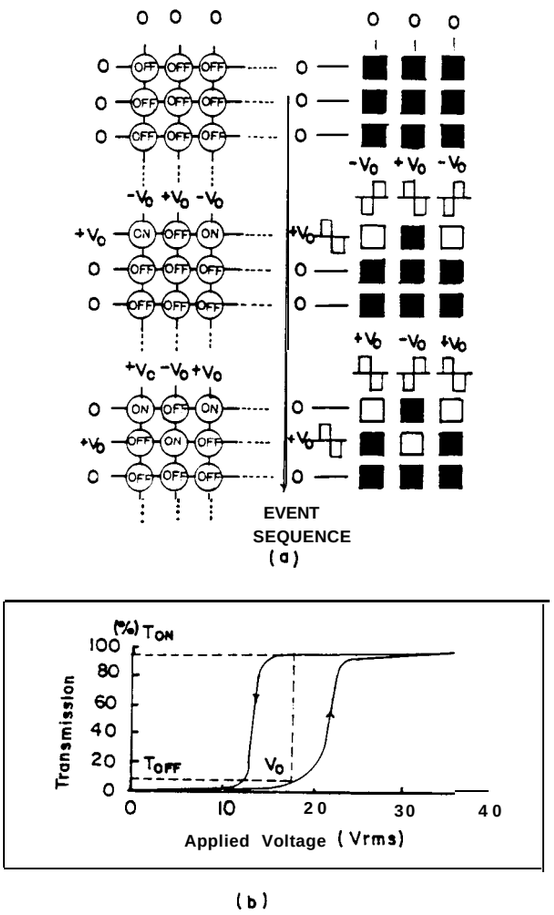


FIG. 8. (a) The proposed driving scheme for a PSCT matrix display. V_0 is the voltage in the vicinity of the center portion of the hysteresis region as shown in Fig. 8(b). The on- and off-pixel have transmittance T_{on} and T_{off}, respectively, as shown in Fig. 8(b). (b) The electro-optical characteristics of a typical PSCT cell operated in the normal mode.

row at a time. A bias voltage V_0 which is in the vicinity of the center portion of the hysteresis region is applied sequentially to each row electrode. This bias voltage is also applied to all columns, except that the phase of each column may be in- or out-phase with respect to that of row's. This results in OV or $2V_0$ across the pixels, respectively. This, in turn, gives off- or on-pixels. Since when the addressing is moved to next row, the voltage across the on- and off-pixel, in the previous row, switches from $2V_0$ to V_0 and 0 to V_0,

respectively. Due to the hysteresis effect, the on- and off-pixel have transmittance T_{on} an T_{off} as shown in Fig. 8(b).

ACKNOWLEDGMENTS

The authors would like to thank Drs. J. W. Doane, D. K. Yang and L. C. Chien of the Kent State University for providing them the monomer material and the use of their facilities. The help from Dr. Y. K. Fung of the Kent State University to obtain the SEM images of the polymer networks is acknowledged. This work is supported by the National Science Council (NSC) of the Republic of China under Grant No. NSC 83-0417-M-006-025. A. Y. -G. Fuh would like to take this opportunity to thank NSC to support him researching in the Kent State University.

REFERENCES

[1] J. L. Fergason, SID Int. Symposium Dig. Tech. Paper, **16,** 68 (1985).

[2] J. W. Doane, N. A. Vaz, B. G. Wu, and S. Zumer, Appl. Phys. Lett. 48, 269 (1986).

[3] P. S. Drazic, J. Appl. Phys. ***60, 2142*** (1986).

[4] S. Zumer and J. W. Doane, Phys. Rev. A43, 3373 (1986).

[5] A. Y. -G. Fuh, British Patent Pending 8713232.

[6] B. G. Wu, J. L. West, and J. W. Doane, J. Appl. Phys. 62, 3925 (1987).

[7] N. A. Vaz, G. W. Smith, and G. P. Montogomery Jr., Mol. Cryst. Liq. Cryst. 146, 17 (1987).

[8] A. Y. -G. Fuh and 0. Caporaletti, J. Appl. Phys. 66, 5278 (1989).

[9] A. Y. -G. Fuh, K. -L Huang, C. -H. Lin, and I. -M. Jiang, Chin. J. Phys. 28, 551 (1990).

[10] G. P. Montogomery Jr. and Nuno A. Vaz, Appl. Opt. 26, 738 (1987).

[11] A. Y. -G. Fuh, T. -C. Ko, Y. -N. Chyr, C. -Y. Huang, B. -W. Tzen, and C. -R. Sheu, Jpn. J. Appl. Phys. 32, 3526 (1993).

[12] A. Y. -G. Fuh, T. -C. Ko, and M. -H. Li, Jpn. J. Appl. Phys. 31, 3366 (1992).

[13] A. Y. -G. Fuh, C. -Y. Huang, C. -R. Sheu, G. -L. Lin, and M. -S. Tsai, Jpn. J. Appl. Phys. 33, 2870 (1994).

[14] A. Y. -G. Fuh, C. -Y. Huang, B. -W. Tzen, C. -R. Sheu, Y. -N. Chyr, G. -L. Lin, and T. -C. Ko, Jpn. J. Appl. Phys. 33, 1088 (1994).

[15] R. L. Sutherland, SPIE Proc. 1080, 83 (1989).

[16] D. -K. Yang, L. -C. Chien, and J. W. Doane, Appl. Phys. Lett. 60, 3102 (1992).

[17] D. -K. Yang, L. -C. Chien, and J. W. Doane, SID 1991 Int. Symp. Dig. 49 (1991).

[18] D. -K. Yang and J. W. Doane, SID 1992 Int. Symp. Dig. 759 (1992).

[19] W. Greubel, Appl. Phys. Lett. 25, 5 (1974).

[20] See, for example, P. G. deGennes, The Physics of ***Liquid Crystals,*** London, Oxford University Press, 1974.

[21] S. C. Jian and H. S. Kitzerow, Appl. Phys. Lett. 64, 2946 (1994).

[22] P. Bos, T. Buzak, and R. Vatne, 1984 Eurodisplay, 7 (1984).

[23] W. E. Holand, 0. Sabni, and P. M. Alt, J. Appl. Phys. 53, 639 (1982).

[24] J. M. Hurd and C. N. King, J. Electronic Mat. 8, 879 (1979).