

Low threshold voltage asymmetric antiferroelectric liquid crystal cells

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Asymmetric antiferroelectric liquid crystal displays (AAFLCD) are attractive since they show a very well defined off state and fast switching time. Moreover, they can be driven by a simple biasless DC compensated waveform. The electrooptical response of an AAFLCD allows for new addressing modes, including quasi-static intermediate greyscales maintained without applying a field and passively addressed multiplexed high-frequency displays and spatial light modulators. A new kind of asymmetric cells have been obtained by using fluorinated block copolymer (FBC) alignment, which enhances surface segregation and provides a low energy surface. In this work we combine FBC alignment with antiferroelectric liquid crystal mixtures containing strongly electronegative fluorinated components. Threshold voltages for the antiferroelectric-ferroelectric phase transition as low as 3 volts are observed. We report the time evolution of the shift of the electro-optical response.

Keywords: antiferroelectric liquid crystals, multistable analogue retardation, alignment layer.

1. Introduction

Antiferroelectric liquid crystals (AFLCs) are attractive for microdisplay applications, because of their fast switching time [1] and passive multiplexability. A passively addressed multiplexed display, is a display in which rows of pixels are being "selected" sequentially by a waveform pulse while synchronously the corresponding data pulses are written to the various columns determining the grey level of each pixel in the selected row. Such a scheme has various requirements:

- various grey levels have to be addressable within a given slot time available to the selection pulse (110 µs for a dual scan XGA display @ 30 frames per second video rate),
- brightest grey levels have to decay slowly in order to achieve a bright display. This is generally achieved by applying a holding, bias, voltage to the pixel after the selection pulse. This voltage will be the same for the entire display. It shall be chosen to be significantly smaller than the switching threshold voltage not to compromise the dark state of the display,
- voltage span needed for generating the full grey scale has to be sufficiently large for the electronics to be able to address various levels, and sufficiently small, not to affect the transmission of pixels in rows that are not being selected.

Often the contrast of the AFLCs display is reduced because of the pretransitional effect produced in symmetric AFLCs by the bias voltage. In order to improve the contrast of AFLC displays, dissimilar alignment conditioning of the two aligning surfaces on opposite plates may be employed. For example, a voltage shift of the AFLC electro-optic response is produced when one of the surfaces is conditioned with a rubbed and cured spin coated polymer such as Nylon6 while the other is coated with non-stoichiometric evaporated oxide such as SiO_x [2]. The voltage shift is easily detectable at low frequency (e.g., 1 Hz) if an AC signal (e.g., triangular) is applied to the cell while observed between crossed polarizers. The typical symmetric AFLC double hysteresis lobes are shifted up to several volts, depending on the AFLC material and the nature and thickness of the aligning layers. Similar asymmetries in the electro-optical response have been reported in nematic liquid crystals, in which one surface has been treated with WO₃ [3–5].

An alternative alignment conditioning generating asymmetric AFLC response with large hysteresis shift has been recently developed in our laboratory. It consists in replacing the thermally evaporated inorganic oxide by a spin coated fluorinated block copolymer (FBC). FBC provides low surface energy layers because the mutual incompatibility of the chemically different polymer blocks enhances surface segregation of the fluorinated polymer block [6]. Fluorinated polymers in fact exhibit very low values of sur-



face tension ($\gamma_s < 15-20$ mN/m) [6–8] and might be exploited for new alignment layers of liquid crystals cells with slippery surfaces. A long term multistable grey level tuning of voltage shift when using the FBC as a low energy surface has been obtained as well [9].

The pretransitional effect in asymmetric cells is remarkably reduced, consequently contrast is improved in quasi static and dynamic conditions, and flickering in video-rate applications [10] arising from unbalanced transmission between positive and negative cycles in symmetric response is avoided. Depending on the shift magnitude, the asymmetric response leads to a number of new addressing modes. Large shifts lead to quasi-static multistable images with no holding voltage (bias), whereas low shifts lead to low power consumption passively-addressed multiplexed video-rate displays [11].

Considerable effort has been applied to optimization of the manufacturing process aiming at achievement of large shifts in asymmetric cells in order to obtain stable greyscales with 0 V holding voltage. In this situation, the driving waveform requires no bias voltage to maintain the grey levels. Biasless driving waveforms make it possible to achieve long term static images without any power consumption. Such a display would be interesting in applications such as mobile electronic equipments (phones, PDAs), information panels etc., where the power consumption is important. Unfortunately, the shift has not been fully stabilized yet, due to migration of ionic charges and charge losses of the cell capacitor. Nevertheless, good progress is being obtained within this area, leading to extremely low (tens of second) refresh rates of the static image.

A number of biasless waveforms has been developed for such displays which significantly simplify the electronic driving [12].

In this work we present electrooptical results of asymmetric cells filled with the induced AFLC [13] materials featuring faster switching times and smaller switching voltages, which offers large and stable shift and shows appropriate working conditions for asymmetric cells in quasi static and dynamic modes with low voltage switching.

2. Experimental

Asymmetric cells were prepared using dissimilar surfaceanchoring on the two sides of the cell. Test cells were prepared with 0.7 mm glass plates, $16 \ 1 \times 1 \ \text{mm}^2$ pixels were imprinted in the ITO coating by photolithography. Eventually, an SiO₂ isolating barrier layer was deposited onto the ITO. The thickness of all cells was about 1.6 µm. Homogeneous planar alignment was induced on one of the ITO coated glass plates by spin-coated Nylon6 dissolved in trichloroethanol (14 g/l). A fluorinated polystyrene block copolymer was spin coated on the opposite glass plate. The cells were filled with a material from W-168 series (Military University of Technology). The series is generated from two synclinic mixtures, one based on protonated compounds and the other based on fluorinated compounds. The antiferroelectric liquid crystal phase



Fig. 1. Temperature dependence of tilt angle measured in a cell filled with the induced AFLC (W-168).

is absent in both of the pure original mixtures, but it is induced when the mixtures are combined as a result of intermolecular interactions [13]. The widest range of AFLC phase occurs approximately at 50:50 molar ratio. The mixture has the following phase transitions Cr 1-3 SmCA 57.4-58.5 SmC 77.8 SmA 88-101 Iso.

Figure 1 shows the measurment of the tilt angle of the induced antiferroelectric liquid crystal. The result shows the tilt angle growing rapidly near SmA–SmC^{*} transition, then saturating at 26° at the temperature range of the antiferroelectric phase.

For comparison, the same type of cell was filled with the commercial antiferroelectric mixture CS-4001 (Chisso) whose components are protonated.

Cells were placed in a hot plate between crossed polarizers and studied in a microscope. The measurement is taken at 35°C at which the material exhibit the antiferroelectric phase. The light output was gathered into an optical fiber bundle and brought to a photomultiplier whose output was sent to a digital oscilloscope. Waveforms were generated by means of an 8-channel ± 100 V arbitrary waveform generator. The whole experimental setup is controlled from a PC computer where waveforms are drawn, greyscales are automatically generated, and output results are collected and plotted.

3. Results and discussion

As usual, in asymmetric AFLC displays, both kinds of cells behave as if a DC signal was superimposed to the external waveform. When the cell is driven with a triangular low frequency AC waveform, a displacement of the full hysteresis curve is observed, resulting in a reduction of the positive threshold voltage (referred to the Nylon side) and a corresponding increase in the negative threshold [Figs. 2(a) and 2(b)]. The difference between the two threshold voltages is approximately 1 V in the case of CS4001 and 5 V in the case of W-168 induced AFLC. Consequently, the positive threshold voltages are reduced compared to the symmetric cell.



Fig. 2. Electrooptical response of asymmetric cell driven with 1 Hz triangular waveform, shifting hysteresis curve measured in cell filled with (a) induced AFLC (W-168) and (b) AFLC CS-4001.

The large shift observed in cells filled with W-168 is stabilised in less than 5 min when applied to a lowfrequency switching (Fig. 3), and remains constant for several hours. In the absence of the electric field, the hysteresis shift turns back to the initial position and thus for final display applications a warming up strategy has to be developed.

These cells show quite interesting properties. The positive hysteresis lobe is so shifted that behaves in practice as a multistable grey scale ferroelectric, rather than antiferroelectric, display developing an analogue greyscale whose dynamic range is compatible with biasless waveforms. Indeed, as seen in Fig. 3, one can develop the full greyscale of the positive lobe in less than 10 V, while the threshold voltage of the negative lobe is above that voltage. Moreover, the holding voltage for the greyscale stabilization is approximately 0 V, since the positive hysteresis cycle is almost centred in the 0 V position. This fact may lead to the possibility of maintaining grey scale static images without any applied power.

The large hysteresis shift achieved in W-168, with fluorinated block copolymers, is particularly significant since this material shows low threshold and saturation voltage, as seen in Fig. 2. These two features combined have led to what is believed to be the first potentially multistable AFLC display, i.e., able to hold any arbitrary grey level with no applied voltage.



Fig. 3. Evolution of hysteresis curves at 1 Hz frequency, measured during 4 hours in asymmetric cell filled with W-168.

The dynamic electrooptical response of both kinds of cells was studied using a basic biasless multiplexing waveform (Fig. 4) consisting of a selection pulse, 0 V bias period over the frame time, and a single well pulse reset that additionally performs the DC-compensation [14]. Greyscale was generated by subtracting data pulses to selection and well pulses.

Figure 5 shows the dynamic electrooptical response at a video frequency of an asymmetric cell filled with protonated mixture CS-4001. This sample has a small voltage shift, and consequently the grey levels are not stabilized by the biasless waveform. Bright states require high addressing voltage (32 V), that may produce side effects such as enhanced ion currents that result in a slow drift of the hysteresis shift with time. The experimental dynamic range (DR) is high as well (7 V). This could be an issue in practical applications, resulting in crosstalk and complicating the design of column drivers for data.

The behaviour of cells filled with W-168 induced AFLC is substantially different, as seen in Fig. 6. A large hysteresis shift allows the grey levels to stabilize without holding voltage. The whole video-rate greyscale is deployed with less than 17 V. The dynamic parameters are also appealing: rise time about 30 μ s, fall time 160 μ s (rise time of CS4001 is lower because the addressing voltage is much higher; fall time is more than twice as much). Dynamic contrast is just fair. Dynamic range, however, is less than 3 V, allowing grey level stabilization in biasless waveforms with very low crosstalk.

At present, further studies are being carried out to relate the concentration of fluorinated components in the AFLC mixture and the voltage shift obtained upon the same alignment surfaces and manufacturing conditions.



Fig. 4. The waveform used for the dynamic characterisation of the AFLC cells. The waveform consists of three parts only, selection pulse (110 μ s), 0 V bias (16000 μ s), and DC-compensation. The waveform is applied to one electrode of the cell; the data is applied to the other.



Fig. 5. Characterization sheet of an asymmetric cell filled with a protonated mixture (CS-4001): (a) the applied waveform used and (b) the electrooptical response. The insert shows the relaxation of the cell. The low transmittance of light indicates that the relaxed anticlinic state is fully achieved at the end of each frame.



Fig. 6. Characterization sheet of an asymmetric cell filled with a protonated mixture (CS-4001): (a) the applied waveform used and (b) the electrooptical response. As in Fig. 4, the insert shows that the cell is fully relaxed by the end of each frame.

4. Conclusions

We have studied asymmetric cells filled with W-168, a low threshold induced AFLC containing fluorinated compound. Large voltage shift in hysteresis curves along with low threshold and saturation voltages leads to the cells behaving as if they were made of a multistable grey scale ferroelectric material rather than an antiferroelectric material. The resulting display can show quasi-static multistable images with no power consumption, and can also be passively multiplexed at video-rate with no holding voltage (bias) and reduced crosstalk.

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References

- A.D.L Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, "Novel phases exhibiting tristable switching", *Jpn. J. Appl. Phys.* 28, L1265 (1989).
- J.M. Otón, J.M.S. Pena, X. Quintana, J.L. Gayo, and V. Urruchi, "Asymmetric switching of antiferroelectric liquid-crystal cells", *Appl. Phys. Lett.* 78, 2422 (2001).
- G. Strangi, D.E. Lucchetta, E. Cazzanelli, N. Scaramuzza, C. Versace, and R. Bartolino, "Asymmetric electro-optical response in a liquid crystal cell containing a layer of amorphous tungsten trioxide", *App. Phys. Lett.* 74, 534 (1999).
- A.L. Alexe-Ionescu, A.T. Ionescu, N. Scaramuzza, G. Strangi, C. Versace, G. Barbero, and R. Bartolino, "Liquidcrystal-electrochromic-material interface: A p-n-like electro-optic junction", *Phys. Rev.* E64, 011708 (2001).
- A.L. Alexe-Ionescu, A.T. Ionescu, N. Scaramuzza, G. Strangi, and C. Versace, "Effects of charge asymmetry in a nematic liquid crystal in contact with an amorphous tungsten trioxide layer", *Mol. Cryst. Liq. Cryst.* 372, 321 (2001).
- X. Li, L. Andruzzi, E. Chiellini, G. Galli, C.K. Ober, A. Hexemer, E.J. Kramer, and D.A. Fischer, "Semifluorinated aromatic side-group polystyrene-based block copolymers: Bulk structure and surface orientation studies", *Macromolecules* 35, 8078 (2002).
- 7. M. Krupers, P.J. Slangen, and M. Möller, "Synthesis and properties of polymers based on oligo (hexafluoropropene

oxide) containing methacrylates and copolymers with methyl methacrylate", *Macromolecules* **31**, 2552 (1998).

- J.M. Corpart, S. Girault, and D. Juhué, "Structure and surface properties of liquid crystalline fluoroalkyl polyacrylates: Role of the spacer", *Langmuir* 17, 7237 (2001).
- N. Bennis, E. Martinelli, G. Galli, M.A. Geday, P.L. Castillo, X. Quintana, and J.M. Otón, "Asymmetric response induced by low energy surfaces in antiferroelectric liquid crystal cells", *Ferroelectrics* (in press, 2006).
- C. Rodrigo, S. Quentel, J. Sabater, X. Quintana, and J.M. Otón, "Flickering and stability in AFLC analogue grey scale", *Ferroelectrics* 178, 55 (1996).
- J.L. Gayo, X. Quintana, N. Bennis, and J.M. Otón, "Addressing waveforms for asymmetric antiferroelectric liquid crystal displays", *Mol. Cryst. Liq. Cryst.* **410**, 451 (2004).
- P.L. Castillo, N. Bennis, M. Geday, F. Beunis, K. Neyts, V. Urruchi, X. Quintana, and J.M. Otón, "Erasing strategies for asymmetric antiferroelectric liquid crystal driving schemes", *Mol. Cryst. Liq. Cryst.* 450, 1 (2006).
- S. Gauza, K. Czupryński, R. Dąbrowski, K. Kenig, W. Kuczyński, and F. Goc, "Bicomponent systems with induced or enhanced antiferroelectric SmC_A^{*} phase", *Mol. Cryst. Liq. Cryst.* 351, 287 (2000).
- X. Quintana, J.L. Gayo, C. Rodrigo, V. Urruchi, and J.M. Otón, "Addressing waveforms for tristable AFLCs in active matrix displays", *Ferroelectrics* 246, 211 (2000).