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Improved Liquid Crystals for Vertical Alignment Applications

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Liquid crystals with a large negative dielectric anisotropy are difficult to align vertically on silicon oxide surfaces and sometimes even on polyimides. An interesting method has been found to generate high quality vertical alignment by doping the host liquid crystal with materials that have a cyanogroup along their long molecular axis. The effect is explained by considering both long range and short range interactions between liquid crystal and the alignment layer. Using this method we propose a way to design new liquid crystal mixtures with large negative dielectric anisotropy that have improved aligning ability for applications requiring vertical alignment. The method also allows for increased birefringence. © 2006 American Institute of Physics. [DOI: 10.1063/1.2209189]

I. INTRODUCTION

Electro-optical devices using vertically aligned liquid crystals with a negative dielectric anisotropy (Δε) have been widely used in many applications because of their high contrast ratio. The vertical alignment of liquid crystals can be obtained on rubbed polyimide thin films, but in some applications such as microdisplays and telecommunication devices, inorganic alignment materials such as silicon oxide (SiOx) are used for better ultraviolet (UV) stability. To achieve lower driving voltage and faster response, liquid crystals with large Δε are preferred. However, it is well known that these types of liquid crystals are very difficult to align vertically on SiOx and sometimes even on polyimides (PIs). In a previous letter we reported that if an appropriate amount of a positive dielectric material, such as 4-pentyl-4-cyanobiphenyl (5CB), is added to the host material that has a large negative dielectric anisotropy, uniform vertical alignment can be easily achieved on both SiOx and PI surfaces. Similar results have been reported by Wen et al. In this paper we propose an explanation for this effect and provide experimental evidence to support this explanation.

II. THEORY

The magnitude of Δε is limited in obtaining uniform vertical alignment on SiOx. We believe that the origin of this problem lies in the interaction between the large lateral dipole moments of liquid crystals with large negative Δε and the SiOx surface. This interaction tends to produce parallel alignment, instead of the desired vertical alignment.

It has previously been shown by Lu et al. that the sign of Δε has a significant effect on the alignment of liquid crystals on SiOx surfaces. Vertical alignment is usually obtained for liquid crystals with a negative Δε while parallel alignment for those with a positive Δε. This groundbreaking observation was explained by the anisotropy of van der Waals interaction related to the dielectric anisotropy of the liquid crystal. As an addition to the theory of Lu et al., we consider the short range dipolar interaction between the liquid crystal molecules and the SiOx surface. This short range interaction becomes non-neglectable when large dipole moments in liquid crystals are present, and it will be maximized when the dipoles are perpendicular to the surface. So for a liquid crystal with positive dielectric anisotropy, a vertical boundary condition is preferred because the dipole is more or less along the long molecular axis, while for a liquid crystal with negative dielectric anisotropy, a planar boundary condition is preferred because the dipole is more or less perpendicular to the long molecular axis. As a result, the orientational preference of long range van der Waals potential and short range dipolar interactions is completely opposite. The final liquid crystal alignment should be determined by the competition between the long range and short range origins.

The idea that liquid crystal alignment may rely on the relative contribution of both long range and short range forces was actually proposed by Dubois-Violette and de Gennes. The authors used Eq. (1) to represent the situation where long range van der Waals force prefers vertical alignment while short range torque prefers planar alignment.

\[ F = \frac{1}{2} \int_{-\infty}^{\infty} u(z) \sin^2 \theta dz + \frac{1}{2} \int_{-\infty}^{\infty} K \left( \frac{d\theta}{dz} \right)^2 dz - \frac{1}{2} W \sin^2 \theta_0, \]  

where \( z \) is the distance from surface; \( \theta(z) \) is the angle of the liquid crystal director tilted away from the surface normal \( [\theta(z)=0 \text{ is along the surface normal, which is the van der Waals force preferred alignment direction for liquid crystal with a negative dielectric anisotropy in our case}] \); \( \theta_0 \) is the value of \( \theta \) at the interface; \( F \) is the total free energy; \( u(z) \) is the van der Waals potential, defined as \( A/\varepsilon^3 \) by de Gennes; \( K \) is the elastic constant of liquid crystal; and \( W \) is the surface anchoring energy that corresponds to the short range interactions.
We believe that a molecule with a strong lateral dipole moment will promote a value of $\theta_0=90^\circ$, while $\theta_0=0^\circ$ will be favored by a molecule with a strong longitudinal dipole moment to achieve maximum short range surface interactions. For a liquid crystal with a large negative $\Delta \varepsilon$, the contribution to the energy from short range interactions may exceed that from the long range van der Waals potential. Therefore vertical alignment becomes difficult to obtain. However, if a dopant material can bind to the SiOx surface preferentially with a vertical orientation and without changing the negative $\Delta \varepsilon$ in the bulk, vertical alignment should be achieved.

Based on this idea, we consider that the addition of a low concentration of liquid crystal molecules with a longitudinal dipole moment may reduce the detrimental short range surface interaction of the lateral dipole moment of materials with a large negative $\Delta \varepsilon$ that causes parallel alignment. In this paper, we investigate this hypothesis and consider if the addition of a material that has a strong longitudinal dipole, thus a positive $\Delta \varepsilon$, can actually allow the use of materials that have a higher negative $\Delta \varepsilon$ in applications requiring vertical alignment.

III. EXPERIMENTS

A. Liquid crystal materials

Two commercial liquid crystal mixtures from Merck (hereafter referred as LC1 and LC2) were used as host materials. LC1 has a relatively high birefringence but a moderate $\Delta \varepsilon$ of $-2.7$. LC2 has a large negative $\Delta \varepsilon$ of $-5.7$ and also a high birefringence, which make it very attractive for many vertical alignment applications. These two fluids were chosen in our experiments mainly because the dopants we used have better solubility in them thus the effect of doping can be demonstrated more obviously.

Several compounds were carefully chosen to be dopants, as shown in Table I. They have similarities as well as differences in many ways for comparison purposes. Specifically, the first five compounds have a cyanogroup along the molecular long axis and thus strong longitudinal dipole moments, but have different molecular lengths, shapes, rings, and linkage groups. Compound 6 has similar structure to compound 5 except that the cyanogroups are in the direction perpendicular to the molecular long axis, so it has a strong lateral dipole moment. Compound 7 (hereafter referred as C3) is the same as compound 6 except that it has a cyclohexyl ring instead of benzene. C3 and compounds that have similar structures have been reported to have huge negative $\Delta \varepsilon$ and are used in commercial liquid crystal mixtures as dopants to increase the magnitude of negative dielectric anisotropy.5,6 Compounds 8–13 are all similar to compound 1 but their functional groups along the molecular long axis are less polar or even nonpolar.

Compound 14 has not only less longitudinal polarity but also a cyclohexyl ring instead of benzene. Except 5CB and 8CB (compounds 1 and 2), all compounds are synthesized in our institute. With these dopants, comparisons of their polarity, molecular shape, dielectric anisotropy, electronic conjugation, and many other properties become possible, which allows us to test our hypothesis.

B. Alignment layer and cell construction

SiOx thin films were prepared by thermally evaporating silicon monoxide (SiO) powders onto glass plates at a medium angle of incidence. The thickness of coating is around 1000 Å, measured by an in situ oscillating quartz crystal. Coated plates were assembled into sandwich cells with anti-parallel evaporation directions on two plates. The cell gap used in the experiments is 20 μm unless otherwise stated in the paper. Liquid crystal mixtures were filled in vacuum by capillary force.
C. Pretilt measurement method

Pretilt angles of liquid crystals were measured on a Nikon polarized light microscope by conoscopic method and crystal rotation method. The relative error between these two methods has been found to be within 0.5°.

D. General examination methods and definition for alignment quality

Liquid crystal cells were examined on a light table between two crossed polarizers. With vertically aligned liquid crystals, cells should always look dark when rotated. For planar cells, bright-dark alternation will be observed when rotated. A cell is defined as uniform if all of the following criteria have been satisfied: (1) More than 80% of the cell area has uniform brightness or darkness observed by eyes; (2) choose five spots in the uniform area that are at the area’s center and four corners. For a planar cell, measure the extinction angle on each spot. The maximum difference between two extinction angles should be smaller than 2°. For a vertically aligned cell, measure the pretilt angle on each spot. The maximum difference between two pretilt angles should be smaller than 1°. Otherwise a cell is defined as nonuniform.

E. Dielectric anisotropy measurement method

20 μm thick empty cells with 1.0 cm² patterned indium tin oxide (ITO) electrodes were made in our laboratory. Accurate cell gap thickness was measured from the interference patterns formed by the reflection from top and bottom surfaces of the gap. The cell uniformity was also carefully examined by measuring the gap thickness at the center and four corners of the patterned electrode. Only those cells with less than 2% thickness variation are used in the experiments. Spin-coated polyimides were used as alignment layers using the standard soft bake hard bake procedure. For vertical alignment, SE-7511 was used, and for planar alignment, SE-2555 was used, both of which were purchased from Nissan Chemicals Inc. Cells were examined and found to be uniform. Pretilt angle of each cell was measured on a center-plus-four-corners basis, as described before. The results show pretilt angle to be less than 1° for planar cells and greater than 89° for vertically aligned cells, all angles measured from the surface.

For each material, the impedances of both planar cell and vertical cell were measured on a Hewlett Packard 4284A 20 Hz–1 MHz precision LCR meter as a function of frequency, ranging from 1 kHz to 1 MHz. Δe was calculated using Eqs. (2)–(5):

\[
Z = Z_r + iZ_i = -\frac{1}{i\omega C} = -\frac{d}{i\omega \Delta \varepsilon_0 \varepsilon},
\]

\[
\varepsilon = -\frac{d}{i\omega \Delta \varepsilon_0 Z},
\]

\[
\varepsilon_r = \frac{dZ_r}{\omega \Delta \varepsilon_0 (Z_r^2 + Z_i^2)}, \quad \varepsilon_i = \frac{dZ_i}{\omega \Delta \varepsilon_0 (Z_r^2 + Z_i^2)},
\]

\[
\Delta \varepsilon = \varepsilon_r - \varepsilon_i = (\text{vertical}) - \varepsilon_r = (\text{planar}),
\]

where \( Z \) is the impedance, \( \omega \) is the angular frequency, \( C \) is the capacitance, \( A \) is the area of the electrode, \( d \) is the cell gap, \( \varepsilon \) is the dielectric constant, and \( \varepsilon_0 \) is the dielectric permittivity of the free space. Subscripts \( r \) and \( i \) stand for real and imaginary parts, respectively. Subscripts || and \( \perp \) stand for parallel and perpendicular to molecular long axis, respectively.

F. Birefringence measurement method

Birefringence of the liquid crystal mixtures was obtained from the optical retardation measurements on the planar cells described in previous subsection. The same center-plus-four-corners examination on cell thickness uniformity and pretilt was performed and only cells with less than 2% thickness variation and less than 1° pretilt (from the surface) were allowed. The optical retardation of a cell is measured by standard Senarmont technique. \( \Delta n \) (birefringence) was calculated from the optical retardation using Eq. (6):

\[
\Delta n = \frac{\Lambda \Gamma}{d},
\]

where \( \lambda \) is the wavelength of light, which is 632.8 nm in our case, \( \Gamma \) is the optical retardation, and \( d \) is the cell gap.

G. Electro-optical curve and respond time measurement methods

Electro-optical curves and respond times of tested cells were measured using a home-built setup and software. The test cell is placed between two crossed polarizers with its surface projection of the easy axis making a 45° angle with the polarization axis. Light coming out from a 632.8 nm He–Ne laser passed through the setup and was detected by a detector. For the \( E-O \) curve, 1 kHz ac square wave was applied to the cell with rms voltage ramping from 0 to 10 V. The transmitted light intensity was detected as a function of the ramping voltage. For response time, 5 V (rms voltage), 1 kHz ac square wave was applied to the cell and released. The detector recorded the transmitted light intensity as a function of time. All measurements were done at 50 °C.

IV. DATA AND RESULTS

A. The effect of dopants with lateral and longitudinal dipole moments

LC1 was used to investigate if the addition of the material that has strong longitudinal dipole can allow the mixtures that have a high negative \( \Delta e \) to align vertically on SiOx. By itself, LC1 assumes uniform vertical alignment on SiOx, but has a small \( \Delta e \) of ~2.7 that is not so attractive for applications. 1-ethoxy-4-(4’-trans-proplyclohexylcarboxy)-2,3-dicyanobenzene (C3, as described in Sec. III A), was added into LC1 to increase the \( |\Delta e| \) and make a better mixture. However, we found that if greater than 4% of C3 was added, the alignment of the mixture deviates from vertical, as can been seen from Fig. 1(a). This effect prohibited us from producing useful mixtures with larger negative \( \Delta e \). 5CB, a dopant with a longitudinal dipole moment, was then added. As
shown in Fig. 1(b), the addition of 5CB allowed mixtures of C3 and LC1 to form vertical alignment that they could not do originally. For the convenience of this paper, we define the minimum weight percentage of 5CB needed to sustain uniform vertical alignment quantitatively described in Sec. III E in a 5CB/C3/LC1 system as the critical amount of 5CB. As can been seen from Fig. 1(b), a different critical amount of 5CB is needed to retain uniform vertical alignment for a different relative ratio of C3 and LC1. Figure 1(c) shows the critical amount of 5CB as the function of the concentration of C3.

It has been observed that the addition of the longitudinal dipole dopant allowed for higher concentrations of the lateral dipole material to be added while still yielding uniform vertical alignment. Figure 2(a) shows that improvement can be achieved in the magnitude of the negative value of $\Delta e$. Also, an improvement of the birefringence is achieved, as shown in Fig. 2(b).

We made two 1.3 $\mu$m thick reflective liquid crystal cells using SiOx as the alignment layer. One was filled in with LC1. Another was filled with the mixture of 88% LC1, 10% of C3, and 2% of 5CB. The electro-optical and time response curves were measured. As shown in Fig. 3, the device with improved liquid crystal mixture has lower threshold voltage and higher optical retardation. The response times are roughly the same, but since the improved LC has higher birefringence, the device could be made thinner to achieve a faster response time.
B. The effect of varying the molecular structure of the dopants

LC2 is an attractive liquid crystal mixture for its high birefringence and high negative $\Delta\varepsilon$. But it has been known to be very difficult to form uniform vertical alignment. In our experiment LC2 formed nonuniform planar alignment on SiOx. We found that with the addition of an appropriate amount of 5CB, the mixture forms uniform vertical alignment. As can be seen from Fig. 4, the concentration of 5CB must be equal to or greater than a critical value to show the effect. But the concentration also has a maximum value beyond which the alignment becomes planar again.

To further explore what criteria of a material are needed for the use as an effective dopant to help generate vertical alignment in liquid crystals with large negative $\Delta\varepsilon$, we added different dopants into LC2. Results are listed in Table I. As can be seen, the longitudinal cyanogroup is directly correlated with a uniform vertical alignment.

V. DISCUSSION

As described in Sec. II, our hypothesis is that there are two origins of the liquid crystal alignment on SiOx: long range van der Waals potential and short range dipolar surface interactions. Those two origins have completely opposite preference in director orientation. Depending on their relative strength, either vertical or planar alignment can be obtained. For a liquid crystal with a large negative $\Delta\varepsilon$, the strong short range interactions between its lateral dipole and SiOx have a big contribution to the total anchoring energy and cause planar alignment. The addition of a small amount of dopant that has a large longitudinal dipole makes the SiOx surface covered with dopant molecules in vertical orientation. As a result, the bulk properties should not change significantly but the surface short range interactions switched its preference in alignment direction. Therefore vertical alignment should be obtained.
The experimental results are consistent with our hypothesis. First of all, pure 5CB with a positive dielectric anisotropy has a planar alignment on SiOx and LC1 with a moderate negative $\Delta \varepsilon$ aligns vertically on SiOx. Second, examples are shown where a liquid crystal with a large negative $\Delta \varepsilon$ aligns parallel to the surface. Third, data from both LC1 and LC2 confirm our hypothesis that adding a small amount of material with strong longitudinal dipole will help in producing vertical alignment on SiOx. Furthermore, results of mixing LC1 with C3 and 5CB also show clear improvements in aligning ability, dielectric anisotropy, and birefringence. This indicates a way to design new liquid crystal mixtures that have large negative $\Delta \varepsilon$, large $\Delta n$, and are also capable to generate vertical alignment that otherwise cannot be easily obtained.

VI. CONCLUSION

We have proposed a hypothesis about the cause of the limitation in the magnitude of the negative $\Delta \varepsilon$ for a liquid crystal to produce vertical alignment on SiOx and shown data that support it. We have also shown that the addition of a positive $\Delta \varepsilon$ material with a strong longitudinal dipole moment can be used to lower this limitation and allow for the application of a material with a larger negative $\Delta \varepsilon$.

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