The Process to Make a Ridge- and Fringe-Field Multidomain Structure Using a Photoimageable Polymer for a Wide Viewing Angle Liquid Crystal Display Application

CHEN CAI,¹ RONALD NUNES,² ALAN LIEN,² EILEEN GALLIGAN,² KALLE LEVON¹

¹ Department of Chemical Engineering, Chemistry and Materials Science, Polytechnic University, Brooklyn, New York 11201, USA

² IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, USA

Received 23 June 1998; accepted 28 September 1998

ABSTRACT: Liquid crystal display (LCD) is very important in the computer industry and many other areas. However, the application of LCD is limited by its narrow viewing angle, compared with a cathode ray tube (CRT) display. In this article a new type of LCD [ridge- and fringe field multidomain homeotropic (RFFMH) LCD], is introduced. In RFFMH LCD, a transparent photoimageable polymer resist is applied to build ridges on each pixel to control the liquid crystal pretilt direction. This photolithographic step imparts a wider viewing angle and simpler LCD production process. In this article the detailed process of building the ridge structure is described, and the thermal stability and chemical resistance of this polymer are studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1197–1203, 1999

Key words: photolithography; photo reaction; RFFMH liquid crystal display

INTRODUCTION

Liquid Crystal Display

Liquid crystal displays (LCDs) have tremendous importance in the computer industry and other industries. Most of the LCDs produced today use either the twisted nematic $(TN)^1$ or supertwisted nematic $(STN)^2$ electrooptical effects (Fig. 1). In the last few years, with the application of thin film transistors (TFT), considerable success has been achieved in notebook and desktop computers, as well as color televisions. Compared with cathode ray tube (CRT) displays, however, it is well known that liquid crystal displays have a much narrower viewing angle.³ With that in mind, vertically aligned (VA) liquid crystal displays (Fig. 2) are being studied, which impart a wide viewing angle.

Correspondence to: A. Lien.

Journal of Applied Polymer Science, Vol. 73, 1197–1203 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/071197-07

Twisted Nematic (TN) and Supertwisted Nematic (STN) Displays

The construction and basic operation of a twisted nematic (TN) display is illustrated in Figure 1. The upper and lower substrate plates (color filter plate and TFT plate), separated by a gap of 5-8 μ m, have lithographically patterned, transparent conductive coatings of Indium-Tin Oxide (ITO) on their inner surfaces. The transparent electrodes have a thin polyimide coating several hundred A thick, which is unidirectionally rubbed by a cloth roller to align the local optic axis (director) of the liquid crystal at the surfaces parallel to the rubbing direction. The upper substrate is rubbed at right angles to the rubbing direction of the lower substrate. In the inactivate state (Fig. 1, left), the local optic axis (director) undergoes a continuous 90° twist in the region between the substrates, indicated by the orientations of the cylinders. TN displays have narrow viewing angle.

A supertwisted nematic display, which has a twisted angle greater than 90°, have some advan-



Figure 1 Principle of operation of a twisted nematic LCD.

tages compared with TN displays, but have even narrower viewing angle.

Ridge- and Fringe-Field Multidomain Homeotropic (RFFMH) LCD

A new type of vertically aligned LCD is demonstrated here that is ridge- and fringe-field multidomain homeotropic LCD (RFFMH LCD). Compared with TN or STN LCDs, RFFMH LCDs have two significant advantages: no rubbing treatment and a wide viewing angle. For TN and STN LCDs, a rubbing treatment is required to align the liquid crystal; however, rubbing may create a static electric charge, possibly damaging the TFT devices and bus line, and at the same time, only a very narrow viewing angle can be achieved. On the other hand, RFFMH LCD does not require rubbing treatment. The alignment of liquid crystal is achieved by building 2 μ m-thick ridges on top of the ITO layer of the color filter. Each pixel of the color filter has one ridge. Figure 3(A) depicts one of the ridge structures we used on the color filter pixel illustrated by the shadowed rectangular area. Other structures were showed in other publications.^{4,5} Figure 3(B), the cross-sectional view of Figure 3(A) along the A-A' line, shows how the ridge structure works. The ridge structure makes the LC molecules near the ridge tilt in the direction away from ridge because the LC molecules



Figure 2 Principle of operation of a vertically aligned LCD.



Figure 3 (A) One ridge structure used in RFFMH LCD demonstration. (B) Cross-sectional view of the structure in (A) and the working principle.

tend to align perpendicular to the homoetropic surface, which covers the ITO layer and ridge structure. When a voltage is applied, the negative anisotropic dielectric LC molecules tend to align perpendicular to the electric field direction. The ridge structure and pixel fringe field work in combination to make the LC molecules in a subpixel tilt in the same direction. The structure of Figure 3(A) will cause the LC molecules in each pixel to tilt in four different directions, resulting in a wide viewing angle.⁴

The slit fringe-field multidomain homeotropic (SFFMH) structure was first demonstrated for passive simple matrix liquid crystal displays by Yamamoto et al. in 1991. The SFFMH mode LCD requires no rubbing treatment and provides wide viewing angles. Various SFFMH structures were proposed for active matrix liquid crystal application by Lien and John in 1993,^{6,7} and one of these structures was demonstrated in a thin-film transistor (TFT) driven LCD panel by Koma et al. in 1995. Recently, Koike et al. showed another type of multidomain homeotropic alignment using a corrugated structure created on both substrate surfaces for each pixel.⁸ The corrugated structure type multidomain homeotropic LCD (with no fringe-field effect) also shows a wide viewing an-



Figure 4 Negative and positive photoresist definition.

gle and requires no rubbing treatment; however, it requires a photolithographic patterning on both the TFT and the color filter substrates. The RFFMH mode LCD in this article needs only one photolithographic step and the combined effect of ridge and fringe field.

Photolithography

In this work, the ridge structures are built on a color filter via microphotolithography. The materials (which is called photoresist) used in microlithography are generally formulated from organic film-forming polymers, photosensitized with small molecular additives. When exposed to UV radiation, such materials will undergo either chain scissioning, crosslinking, or molecular rearrangements, thereby creating a solubility difference between the exposed and the unexposed areas of the polymer. In a subsequent step called development, the more soluble regions are selectively removed. There are two kinds of photoresists: positive and negative. In positive photoresists the exposed regions become soluble, whereas in negative photoresists the exposed regions become insoluble (Fig. 4).

EXPERIMENTAL

The fabrication process of RFFMH LCD is similar to the process of conventional LCD, both having a color filter substrate and a TFT substrate with a $5-\mu$ m gap between them. The major difference is that, in the process of RFFMH LCD, there is a photolithographic step to fabricate ridges on the color filter instead of rubbing the surfaces of the color filter and TFT substrates in the process of conventional LCD. In this photolithographic step, a negative photoresist, Shipley XP-9595 photoimageable LCD top coat, which contains an acrylic copolymer, was used. This polymer solution was spin coated on top of the Indium-Tin Oxide (ITO) layer (acting as the electrode) of the color filter substrate.

The color filter substrates were first treated with hexamethyldisilazane(HMDS, $[(CH_3)_3Si]_2NH)$ adhesion promoter in a YES oven before resist coating. A continuous film of this polymer was formed and was softbaked on a hot plate. Exposures were made using an MRS 5000 1HT Panelprinter, a g-line exposure tool, with wavelength centered at 436 nm. A designed mask was used with the designed geometries.

The following step is the post-exposure bake (PEB) to insolubility of the exposed regions. The images were developed by immersion in Shipley LDD-26W developer (aqueous solution of Tetramethyl Ammonium Hydroxide, TMAH, less than 3 wt %) for a predetermined time. The final lithographic step was postbake (or hardbake) to complete the crosslinking reaction and harden the resist. The next steps were coating polyimide and LCD assembling. Nissan 1211 polyimide was used in this process to cover the polymeric ridges.

To get the optimal thickness of photoresist film (or ridge), several different thicknesses (1.5, 2, 2.5, and 3 μ m) were tried. Two micrometers was found to be the minimal thickness to obtain stable liquid crystal domain. To determine the correct spin speed, a spin curve was made by spin coating the polymer at different speeds and measuring the film thickness with a profilometer (Tencor P-1 Long Scan Profiler).

To determine the softbake conditions, Differential Scanning Calorimetry analysis of the polymer powder was done on TA2920 DSC instrument, and Thermogravimetric Analysis was done on Perkin-Elmer TGA.

RESULTS AND DISCUSSION

Spin Speed

From the spin curve (Fig. 5), 1300 rpm spin speed was needed to obtain a 2 μ m-thick polymer film, which was measured after postbake because the polymer film shrinks about 10% during postbake.

Softbake Conditions

Softbake (or prebake) involves the physical removal of the casting solvent without degradation



Figure 5 Spin curve of XP-9595.

of the polymer components. By removing the casting solvent from the film, a solid state is formed that prevents mixing of the exposure products with the unexposed zone. For efficient solvent removal, the prebake temperature should be above the T_g of the polymer, but should not be high enough to decompose the photosensitive components (T_d) . Above the T_g , the solvent diffuses rapidly out of the film (Fig. 6).⁹ T_g of this polymer is about 40°C, as shown in the DSC curve (Fig. 7), and the T_d is about 280°C (TGA curve, Fig. 8). The solvent of this photoresist is ethyl lactate, which has boiling point as high as 154°C. Several different softbake temperatures were tried, and TGA was used to check the amount of remaining solvent. To avoid inefficiently removing of solvent when the temperature is too low, and crosslinking reaction in this polymer at too high a temperature, 90°C for 5 min was used as the softbake conditions. The TGA curve (Fig. 8) confirms that there is only a small amount of



Figure 6 Drying of photoresist (rate of outgassing) film heated below and above T_{g} .



Figure 7 DSC curve of XP-9595 photoresist (solid).

solvent (less than 3 wt %) left under this softbake condition.

Exposure, Post-exposure Bake (PEB), and Development

Photo-reaction (Cationically Initiated Thermal Crosslinking Reaction)¹⁰







Photoresist was exposed with varying dosage from 110 to 550 mJ/cm² in increments of 20 mJ/



Figure 8 TGA curve of XP-9595 photoresist (solid).



Figure 9 The thickness of resist film after different development time and rinse.

 $\rm cm^2$. Under lower dosage, not enough of the photogenerated acid was formed, and image integrety was lost on both width and thickness. On the other hand, too high a dosage resulted in a wider than designed ridge structure. An optimal dosage of 350 mJ/cm² was found to yield the best result.

Post-exposure Bake

PEB conditions were determined by varying PEB temperatures from 100 to 125° C in increments of 5°C, and PEB time from 1 to 5 min. At a lower temperature and shorter PEB time, the crosslinking reaction was not efficient, causing image lost. However, a higher PEB temperature and longer PEB time yielded lower photospeeds (more efficient use of photogenerated acid) but poorer resolution, which is consistent with the chemistry reaction in the PEB step. An optimal condition was chosen at 115°C for 2 min.

Development

At room temperature, an unexposed $2-\mu m$ photoresist film (with softbake and PEB bake) was developed in a Shipley LDD-26W developer for different times, and the thicknesses of the remaining film were measured with a profilometer (Tencor P-1 Long Scan Profiler). The curve of the developing time vs. the thickness of the remaining film was then made (Fig. 9). To completely remove the unexposed film, 140 s was needed.

The resist was hardbaked at 220°C for 16 min to harden the ridges.

Under the combination of these conditions, the desired profile was obtained (Fig. 10).

The Reproducibility and Reliability of the Photolithographic Step

The height and width of the ridges were measured as 1.9 $(\pm 5\%)~\mu m$ and 6.0 $(\pm 10\%)~\mu m,$ re-



Figure 10 SEM picture: cross-sectional view of one pattern structure.

spectively. These small variations will not affect the performance of the whole panel, and the ridge layer still can be treated as a uniform layer.

A dust-free environment and careful operation can keep defect percentage very low. A whole color filter substrate (about 4 million pixels) has only a few defects (less than five pixels). This promises the reproducibility and reliability of the photolithographic step.

Chemical Resistance, Thermal Stability, and Optical Transparency

Because the photoresist stays inside the liquid crystal display, its chemical resistance, thermal stability, and optical transparency become very important. During coating the polyimide over the ridges, no interfacial problems were observed, which means that the photoresist has good chemical resistance. The photoresist has excellent thermal stability (Fig. 8, TGA curve). The optical



Figure 11 UV spectrum of 2 μ m XP-9595 film.



Figure 12 A scheme of polyimide layer.

transmission of this photoresist film as a function of wavelength is shown in Figure 11. The photoresist film has a small effect on the optical transmission, but is acceptable.

Polyimide Coating Process

To achieve a thin layer of polyimide, Nissan 1211 polyimide was diluted by its original solvent (commercial). Then the diluted Nissan 1211 polyimide was coated on the top of the ridge profile to form a polyimide layer with a thickness of about 500 Å. This kind of polyimide has a high density of alkyl sidechain, which vertically aligns nematic liquid crystal molecules (Fig. 12).

Other Fabrication Process

After coating the polyimide, the plate was assembled with a TFT plate (which was also coated by a polyimide layer). Plastic spacer balls (5 μ m) were used to form the cell gap, and a UV-curable epoxy glue was used to glue these two plates together. Finally, this panel was filled with a negative anisotropic nematic liquid crystal by vacuum injector.

Viewing Angle Measurement

The contrast ratio curves of RFFMH and TN LCDs are shown in Figures 13 and 14. The contrast ratio is the ratio of transmitted luminance of the bright state to the dark state. Every curve on these diagrams corresponds to a given contrast ratio at various viewing directions characterized by a polar and an azimuthal angle. The center of the diagrams refer to on-axis viewing, and the periphery to 50° off-axis viewing. By comparing Figures 13 and 14, it is seen that, for a certain contrast ratio number, the viewing angle of RFFMH LCD is much wider than that of TN LCD, and also much more symmetric.



Figure 13 The measured viewing angle of a RFFMH mode LC cell. The contour levels are contrast ratios of 10, 20, 50, 150, 200, 400, 700, and 1000.

CONCLUSION

The wide viewing angle ridge- and fringe-field multidomain homeotropic LCD has been demonstrated by using negative photoresist to build ridges on a color filter to control the LC molecules tilting direction instead of rubbing. This imageable photoresist can be operated by controlling exposure, bake temperature and time, and development. This advantageous LCD will possibly replace the conventional LCD in computer industry and other industries in the future.

We would like to express our gratitude to Richard John from IBM T. J. Watson Research Center for his expert advice in LCD fabrication process, and Mary Beth Rothwell (also from IBM T. J. Watson Research Center) for taking SEM pictures.



Figure 14 The measured viewing angle of a TN mode LC cell. The contour levels are contrast ratios of 5, 10, 20, 50, 100, 150, 200, and 250.

REFERENCES AND NOTES

- 1. Schadt, M.; Helfrich, W. Appl Phys Lett 1971, 18, 127.
- 2. Scheffer, T. J.; Nehring, J. Appl Phys Lett 1984, 45, 1021.
- Lien, A.; Takano, H.; Suzuki, S.; Uchida, H. Mol Cryst Liq Cryst 1991, 198, 37.
- Lien, A.; Cai, C.; Nunes, R.; John, R. A.; Galligan, E.; Colgan, E.; Wilson, J. Jpn J Appl Phys Part 2 1998, 37, L597.

- Lien, A.; Cai, C.; Nunes, R.; John, R. A.; Galligan, E.; Colgan, E.; Wilson, J. 1998, SID 98, 1123.
- 6. Lien, A.; John, R. A. Euro Display'93 1993, 21.
- Lien, S.-C. A; John, R. A. U.S. Pat. 5,309,264 (1994).
- Koike, Y.; Kataoka, S.; Sasaki, T.; Tsuda, H.; Takeda, A.; Ohmuro, K. IDW'97 1997, 159.
- 9. Moreau, W. M. Semiconductor Lithography; Plenum Press: New York, 1988.
- Brainard, R. L.; Perkins, M. E.; Bacchetti, L. F.; doCanto, M.; Pavelchek, E. K.; Cernigliaro, G. J.; Simon, E. S. SID 95 Digest 1995, 783.