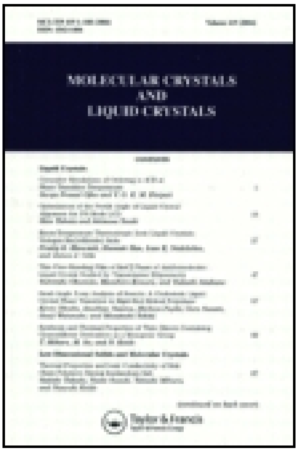

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This paper introduces zirconia (ZrO_2) use in liquid crystal (LC) alignment for uniform and effective LC orientation. We used a conventional rubbing process to induce LC alignment. As a result, uniform LC alignments were achieved in all samples with ZrO_2 nanoparticles from 0.01 wt% to 0.3 wt%. Pretilt angles of LCs on ZrO_2 nanoparticles doped LC alignment layers slightly increased as the percentage of ZrO_2 nanoparticles rose. However, contact angles were almost the same. When twist-nematic (TN) LC cells used LC alignment layers with ZrO_2 nanoparticle content of 0.1 wt%, best performance was shown. Finally, it is shown that ZrO_2 nanoparticles doped LC alignment layers have more thermal budget than pristine ones in thermal stability test.

Keywords ZrO_2 nanoparticle; rubbing; liquid crystal alignment; doping concentration

Introduction

Thin film transistor (TFT) liquid crystal displays (LCDs) are widely employed in flat panel displays such as notebook computers, monitors, and televisions because they provide excellent resolution quality, low power consumption, and high performance. However, the performance and the fabrication processes of TFT-LCDs are still being improved.

In improving the performance of TFT-LCDs, the combination of nanomaterials and nanotechnology into LCDs has attracted great attention due to their unique electro- and magneto-optic properties and new display applications [1–6]. Many research groups have

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found that liquid crystal (LC)-nanoparticles mixtures showed novel electro-optical properties such as memory effect [1, 2], frequency modulation properties [3], low threshold voltage [4], and fast response time [5]. Hwang et al. showed that the pretilt angles of LC molecules can be controlled by using conventional polyimide (PI) alignment material doped with different concentrations of polyhedral oligomeric silsequioxanes (POSS) nanoparticles [6].

On the other hand, nanoparticle use in LC alignment layers such as polyimide (PI) and [3-(trimethoxysilyl)propyl]octadecyl-dimethylammonium chloride (DMOAP) has not been studied much. Occasionally, TiO_2 nanoparticle doped PI was studied as an optical waveguide material [7] and effects of molecular orientation and birefringence of magnetic nanoparticle/PI composites were studied [8].

In this study, we demonstrated electro-optical properties of LC system using dispersed ZrO_2 nanoparticles in PI layers and rubbing process. ZrO_2 have been deployed in various devices such as electrodes [9], solar cells [10] and transparent thin films [11], because they offer many advantages including high refractive index, useful optical properties, excellent thermal stability and chemical inertness [12]. Therefore, we employed ZrO_2 nanoparticles as a dopant to LC alignment layer to improve characteristics of LCDs.

Experimental

Before preparing the LC alignment layer, an ITO-coated glass was cleaned with a supersonic wave in a bath using acetone, isopropyl alcohol, and deionized water solution for 10 min and then air-dried. We made a uniform LC alignment layer composed of homogeneous PI (SE-150, Nissan Co. Ltd) and ZrO_2 nanoparticles by spin-coating on an ITO-coated glass. For the ZrO_2 nanoparticles doped LC alignment layer, the conditions of prebaking and imidizing were 80°C for 10 min and 230°C for 1h, respectively. ZrO_2 nanoparticles used in this paper were synthesized as described previously [13]. The thickness of the ZrO_2 nanoparticles doped LC alignment layer was approximately 50 nm, which is sufficient to operate an LC system normally. The ZrO_2 nanoparticles doped LC alignment layers were rubbed using a machine equipped with a nylon roller (Y_o-15-N, Yoshikawa Chemical Industries Co. Ltd.) to obtain uniform LC configuration. The definition of the rubbing strength (RS) was given in a previous paper [14]. The LC cells were fabricated as a sandwich type with anti-parallel structure with the cell gap of 60 μm to observe LC texture and to measure UV transmittance, pretilt angles and thermal stability. Positive nematic LCs ($T_c = 72$°C, $\Delta\varepsilon = 8.2$, $\Delta n = 0.0987$, MJ001929 from Merck) were used. We confirmed the alignment statements using a photomicroscope (Olympus BXP 51). UV transmittances of LC cells with pristine and ZrO_2 nanoparticles doped PI layers were measured respectively by UV visible near infra-red (UV-VIS-NIR) spectrometer (SHIMADZU UV-3101PC). The pretilt angles of the LC cells were measured using crystal-rotation method (Autronic TBA-107) at room temperature. For measuring voltage-transmittance characteristics, TN cells with the cell gap of 5 μm with differnt ZrO_2 nanoparticle content were fabricated. Voltage-transmittance characteristics of TN cells were measured using a LCD evaluation system (LCMS-200). Finally, contact angles were measured by the sessile drop technique at room temperature using contact angle analyzer (Scientific Gear Pheonix 300) to reveal the effect of ZrO_2 nanoparticles on the LC orientation.

Results and Discussion

The LC alignment statements for LC cells with ZrO_2 nanoparticles doped PI layers were analyzed as a function of ZrO_2 nanoparticle content. Figure 1 shows photomicrographs

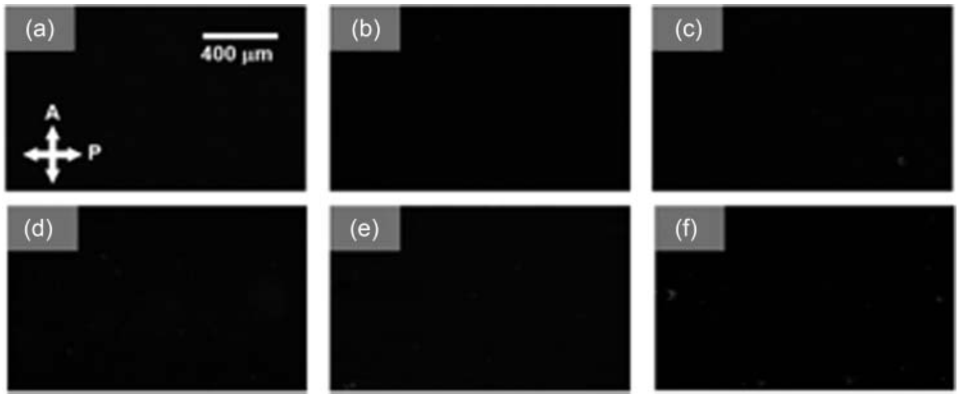

Figure 1. Photomicrographs of LCs on ZrO_2 nanoparticle doped LC alignment layer surfaces subject to rubbing treatment (in crossed Nicols): (a) 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.2, and (f) 0.3 wt%.

of LCs on ZrO_2 nanoparticle doped LC alignment layer surfaces subject to rubbing treatment (in crossed Nicols). As a reference, pristine counterparts were also prepared. Good alignment was observed in all LC cells. Clear and stable images suggest that the ZrO_2 nanoparticle doped LC alignment layer is appropriate for aligning LC molecules with the transparency property. However, LC alignment statements became worse with the increase of ZrO_2 nanoparticle content more than 5 wt%. Beyond ZrO_2 nanoparticles content of 5wt%, nanoparticle agglomerations were formed in some places. The defects of LC cells might be occurred by nanoparticle agglomeration. Therefore, concentrations of ZrO_2 nanoparticles should be set to less than 0.5 wt%.

Figure 2 shows the UV transmittance spectra of pristine and ZrO_2 nanoparticle used LC cells. The transparencies of the LC cell with ZrO_2 nanoparticles doped PI layers are comparable to the transparency of the pristine counterpart. Over the wavelength range of 420–780 nm, the average optical transmittances of the pristine and ZrO_2 nanoparticles

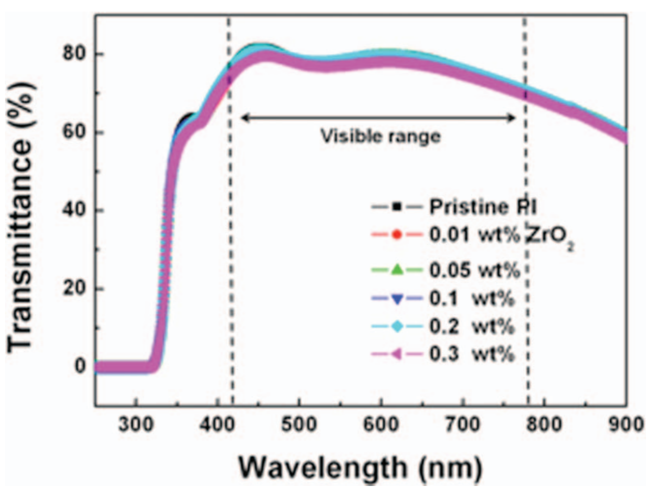

Figure 2. UV transmittance spectra of the pristine and ZrO_2 nanoparticles used LC cells.

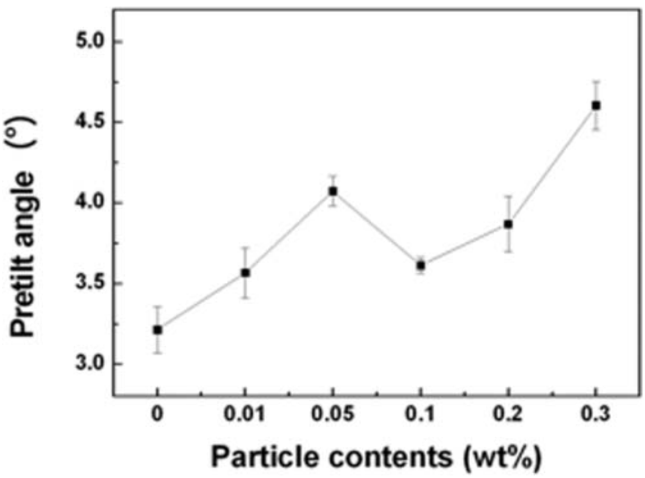

Figure 3. The pretilt angles of the LCs on ZrO_2 nanoparticles doped LC alignment layer as a function of ZrO_2 nanoparticle content.

doped LC alignment layer were 77.6–78.3%. This means ZrO_2 nanoparticles are well dispersed among the PI layer and it did not affect the transparency of the LC cell. Also, this result was correlated to the photomicrographs as shown in Fig. 1. Therefore, it may conclude that LC cells can be enhanced by ZrO_2 nanoparticles doped LC alignment layer with no loss of transparency.

Figure 3 shows the pretilt angles of the LC on a ZrO_2 nanoparticles doped LC alignment layer as a function of concentrations of ZrO_2 nanoparticles. The pretilt angles generated were dependent on the ZrO_2 nanoparticle content significantly. Variation of pretilt angles from 3.3° to 4.5° indicates that ZrO_2 nanoparticle concentrations affect LC orientation on LC alignment layer. However, the mechanism of LC orientation on ZrO_2 nanoparticles doped alignment layer have not been elucidated anywhere before. LC orientation with regular pretilt angle might be occurred by fine changes in topographical shape of the LC alignment layer because of doping of the layer with ZrO_2 nanoparticles.

We measured contact angles of DI-water on pristine and ZrO_2 nanoparticles doped LC alignment layers to analyze correlation between pretilt angles and surface energy. Figure 4 shows the measurements of the contact angles for each observed photomicrograph of the pristine and ZrO_2 nanoparticles doped LC alignment layer surfaces. Regardless of concentrations of ZrO_2 nanoparticle, we observed that the contact angles were analogous to one another. In previous studies, an inverse relationship is shown between pretilt angles and contact angles [15] because the contact angle is closely related to the surface energy; if a certain LC alignment layer has high surface energy, it becomes aligned homogeneously. However, our study did not show significant changes in contact angles. This result is attributed to doping ZrO_2 nanoparticles in the LC alignment layers. More ZrO_2 nanoparticles can make much improvement in properties of alignment layer, but it also brings the degradation of display quality such as transparency.

The variation of pretilt angles might affect electro-optical properties of TN LC cell such as voltage-transmittance characteristics and thermal stability. We fabricated TN LC cells with ZrO_2 nanoparticles doped LC alignment layer with different ZrO_2 nanoparticle content to examine the voltage-transmittance characteristics. For comparison, we also fabricated a

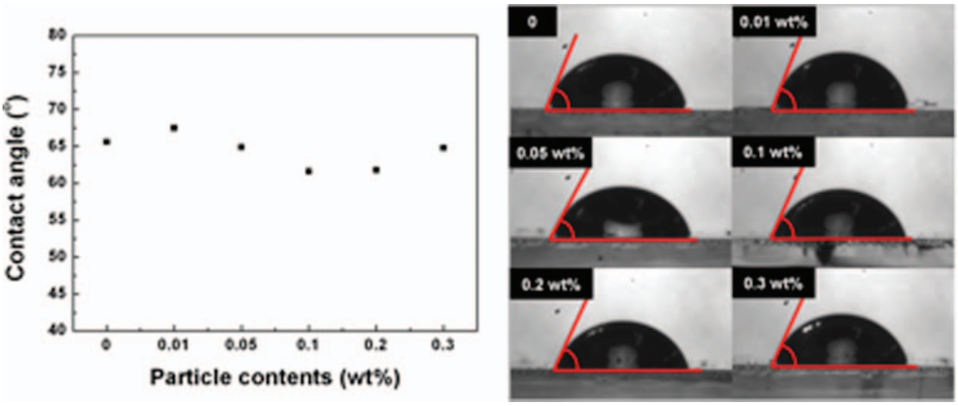

Figure 4. The measured contact angle values on ZrO_2 nanoparticles doped LC alignment layer surfaces and the observed photographs of the contact angles.

conventional TN LC cell with a pristine PI layer. Figure 5(a) shows the voltage-transmittance curves of the TN LC cells. As can be shown, voltage-transmittance curves of TN LC cells seemed to be traced out the curves of each others. However, there was a slight difference in threshold voltage of TN LC cells. In Fig. 5(b), the TN LC cell using ZrO_2 nanoparticles content of 0.1 wt% had lowest threshold voltage of 2.0 V. Decreasing threshold voltage of TN LC cell makes it possible for LC system to operate with lower power consumption. Through repeated measurements, ZrO_2 nanoparticle content of 0.1 wt% was found to be an optimal value to improve TN LC cells.

Figure 6 shows the photomicrographs of the LC cells to examine the relationship between the ability of the LCs to maintain their orientation and the thermal stability. For measurement of the thermal stability, the LC cells were annealed from 90°C to 240°C with increments of 30°C for 10 min. All images were clear without any defects until annealing temperature of 180°C. However, the LC orientation on pristine PI surface was destroyed at 210°C. This result indicates that doping with ZrO_2 nanoparticles helps to disperse heat in the LC cells because effective surface areas of ZrO_2 nanoparticles increased as the amount of ZrO_2 nanoparticles dispersed in PI matrix increased. Doping with ZrO_2 nanoparticles

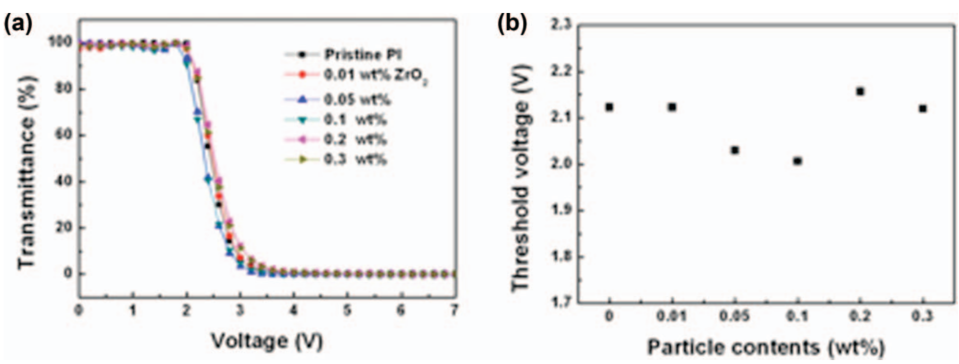

Figure 5. (a) Voltage-transmittance curves and (b) threshold voltage of the TN LC cells with the pristine and ZrO_2 nanoparticles doped LC alignment layer.

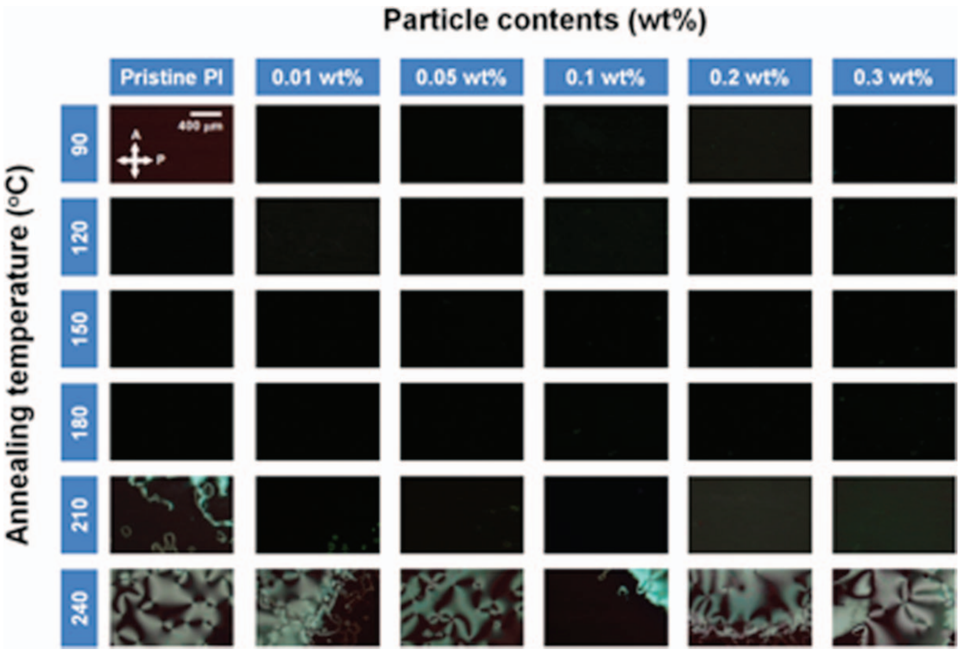

Figure 6. Photomicrographs of each LC cell with the pristine and ZrO_2 nanoparticles doped LC alignment layers. Each cell was annealed using different annealing temperatures to examine thermal stability.

could reduce the fluidity of PI chain due to high affinity with PI matrix. Therefore, LC cells with ZrO_2 nanoparticle doped LC alignment have high thermal budget.

Conclusions

In summary, ZrO_2 nanoparticles doped LC alignment layer for effective LC orientation was studied with successful results. The LC molecules were aligned homogeneously and uniformly on ZrO_2 nanoparticles doped LC alignment layer surfaces. Although pretilt angles of LCs increased as ZrO_2 nanoparticles content increased, contact angles remained the same. Considering the results for voltage-transmittance of TN LC cells, TN LC cells with ZrO_2 nanoparticles doped LC alignment layer were competitive over conventional TN-LCDs. Doping ZrO_2 nanoparticle content of 0.1 wt% makes it possible for TN LC cell to operate with low power consumption. In addition, the test of thermal stability revealed that ZrO_2 nanoparticles doped LC alignment layers have more thermal budget than pristine ones. Also, since this method employed the conventional PI materials, it could be adopted in the conventional LCD fabrication process.

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