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### Electro-optical properties of liquid crystal displays based on the transparent zinc oxide films treated by using a rubbing method

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#### ABSTRACT

Liquid crystal (LC) alignment on inorganic films has been found to be affected by surface modification via ion-beam irradiation. In this study, ZnO films treated by rubbing with a velvet cloth were shown to be capable of aligning LC molecules in the direction of the rubbing. Uniform and homogeneous LC alignment was achieved on the rubbed ZnO films. By analysing the optical axes before and after the rubbing treatment, we confirmed an increase in the anisotropy of the ZnO films; this optical anisotropy contributed to the uniform orientation of LC molecules. Further, the electro-optical characteristics of the twisted nematic cells based on ZnO films were superior to those based on conventional polyimide layers. Our results indicate that the rubbing approach could be applied in the fabrication of high-performance LC displays.

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#### 1. Introduction

The alignment of liquid crystal (LC) molecules is still of great interest for both fundamental research and industrial applications [1,2]. LC alignment strongly depends on the interactions between LC molecules and solid-substrate surfaces [3–7]. Achieving uniform alignment of LCs with a regular pretilt angle on the alignment film is essential for electro-optical performance in LC displays (LCDs) [8–10]. Intensive research into the use of various types of alignment layers comprising functional materials such as polymers, metal oxides and anisotropic nanostructures has been conducted, with the goal of obtaining uniform LC alignment [11–15]. Of the several candidates for LC alignment layer materials, high- $\kappa$  inorganic materials are of particular interest because they

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can enhance the electro-optical (EO) characteristics in LCD applications by increasing the effective voltage across the LC cells [16,17]. However, there is a major limitation in using them: uniform LC alignment can only be achieved on the inorganic films if surface modifications are made using expensive alignment methods such as ion-beam (IB) irradiation or under special deposition conditions [16,17]. Recently, we reported that uniform LC alignment was achieved on solution-derived SnO<sub>2</sub> films without any alignment technique [18].

Among the various known alignment techniques, which include rubbing, SiO oblique deposition [19], ultraviolet photoalignment [20], nanoimprint lithography [11] and IB irradiation [12,13], the rubbing process [21] has attracted considerable attention because of its relative simplicity, cost effectiveness and reliability. Therefore, in this study, we employed solution-derived ZnO films as an LC alignment layer using a conventional rubbing process and achieved uniform alignment. To determine the effect of the rubbing treatment on the ZnO films, we conducted physicochemical analyses using contact angle measurements, atomic force microscopy (AFM)

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and optical retardation measurements. In addition, the rubbed ZnO films were applied in twisted nematic (TN) cells to assess their applicability to LCDs.

#### 2. Experimental

#### 2.1. Preparation of ZnO via solution process

ZnO films were prepared on indium tin oxide (ITO)-coated glass substrates (Samsung Corning 1737: standard 32 mm  $\times$  22 mm  $\times$  1.1 mm, sheet resistance 10  $\Omega$  sg<sup>-1</sup>) by spin coating. The substrates were cleaned by sequential ultrasonication in acetone, methanol and de-ionized (DI) water for 10 min each and then dried with N2 gas. The ZnO precursor solution was 0.5 M zinc acetate dihydrate in 2-methoxyethanol with monoethanolamine as a stabilizer. The solutions were stirred at 200 rpm for 30 min at 60 °C using a magnetic stirrer hotplate to ensure homogeneity before ageing at room temperature for at least 1 day. The ZnO solutions were then deposited on ITO-coated glass by spin coating at 3000 rpm for 1 min. Residual solvent was removed from the ZnO films by prebaking at 200 °C for 10 min. Finally, the ZnO films were sequentially annealed in a furnace at temperatures of 100 °C, 200 °C, 300 °C, 400 °C and 500 °C for 1 h each.

#### 2.2. Rubbing treatment on prepared ZnO films

The ZnO films were rubbed using a machine equipped with a nylon roller (NMS-RB, Namil motion system). The rubbing strength was conventionally optimized and set at 300 nm.

#### 2.3. Fabrication of liquid crystal cells based on ZnO films

The resultant substrates were used to fabricate empty cells with configurations that were anti-parallel for LC cells and perpendicular for TN cells, with cell gaps of 60  $\mu$ m and 5  $\mu$ m, respectively. The positive LCs (Tc = 72 °C,  $\Delta\epsilon$  = 8.2 and  $\Delta$ n = 0.077; MJ001929, Merck Corp.) were injected into each cell by capillary action in the isotropic phase.

#### 2.4. Measurement of LC alignment states and EO performance

The LC alignment characteristics were observed under a photomicroscope (BXP 51, Olympus), and the pretilt angles were measured by the crystal rotation method (TBA 107 Device, Autronic). The contact angles of the ZnO surfaces were measured by the sessile drop technique with DI water and diiodomethane using a phoenix 300 surface angle analyser and were analysed with the IMAGE PRO 300 software. The surface morphology of the ZnO films was analysed using AFM (XE-Bio, Park Systems). To determine the optical anisotropy, we measured the optical retardation (REMS-100, Sesim). The EO characteristics of the TN cells employing rubbed ZnO films were measured using an LCD evaluation system (LCMS-200, Sesim).

#### 3. Results and discussion

#### 3.1. Evaluation of the LC alignment state

Fig. 1 shows photomicrographs of the LC cells employing rubbed ZnO films as a function of growth temperature. The inset shows an LC cell with an anti-parallel configuration. The LC molecules aligned uniformly and homogeneously on the rubbed ZnO films, irrespective of growth temperature.

The uniform LC alignment on the rubbed ZnO films was also confirmed by measuring the pretilt angles of the LC molecules on the rubbed ZnO films using the crystal rotation method. Fig. 2(a-e)shows the oscillations in the transmittance of each LC cell for  $\pm 70^{\circ}$ latitudinal rotation, which were used for calculating the pretilt angles of the LC molecules on the rubbed ZnO films. When the measured (red line) and simulated (red line) curves are identical, the LC alignment is uniform and precise calculation of the pretilt angle of the LC molecules is possible. As can be observed from Fig. 2, the well-matched transmittance curves indicate that the pretilt angle of the LC molecules on the rubbed ZnO films is determined with high reliability. In addition, these results indicate that uniform LC alignment on the rubbed ZnO films was achieved, irrespective of growth temperature. The pretilt angles of the LC molecules on the rubbed ZnO films were found to be in the range of 0.15°-0.34°, with low error values, as shown in Fig. 2(f). The pretilt angles of the LC molecules were relatively constant with respect to changes in the growth temperature of the ZnO films.

## 3.2. Contact angle measurement and surface investigation on the *ZnO films*

The effect of the rubbing treatment on the ZnO films was investigated by means of contact angle, surface morphology and optical retardation measurements (Fig. 3). Table 1 shows the variation in the contact angles and surface energies of the rubbed ZnO films before and after the rubbing treatment. The surface energies were calculated from the DI water and diidomethane contact angles according to the Owen–Wendt equation [22]. The average contact angles of untreated ZnO films and rubbed ZnO films were 84.72° and 83.86° for DI-water and 33.61° and 37.12° for



Fig. 1. Photomicrographs of LC cells based on ZnO films as a function of growth temperature. 'A' denotes 'analyser' and 'P' denotes 'polarizer'. The inset shows an LC cell with an antiparallel configuration to observe the LC alignment state and pretilt angle.

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