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Spontaneous liquid crystal alignment on solution-derived nanocrystalline tin-oxide films

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Abstract

We investigated the use of solution-derived nanocrystalline SnO₂ films to promote the self-alignment of liquid crystal (LC) molecules. Uniform and homogeneous LC alignment was spontaneously achieved by using these substrates. LC molecules with a preferred orientation were aligned along the filling direction, and the LC alignment was maintained via van der Waals force by nanocrystals of the solution-derived SnO₂ films. This phenomenon did not occur in amorphous-phase SnO₂ films. Nanocrystalline SnO₂ films were grown at annealing temperatures greater than 400 °C. Although the average transmittances of the SnO₂ films degraded slightly as the annealing temperature increased, the values were similar to those of conventional polyimide films. Electrically controlled birefringence mode cells fabricated using the solution-derived nanocrystalline SnO₂ films exhibited superior electro-optical characteristics, indicating that this approach will allow the fabrication of advanced LC displays with high performance through a simple fabrication process.

Keywords: nanocrystalline tin-oxide (SnO₂), liquid crystal alignment, self-alignment, solution processing.

1. Introduction

The uniform alignment of liquid crystal (LC) molecules in a uni-directional orientation is considered to be a core technological requirement in the fabrication of liquid crystal displays (LCDs). Intensive research on the use of organic or inorganic films as LC alignment layers has been conducted to obtain uniform LC alignment via various alignment techniques¹⁻¹⁵. The rubbing method is conventionally used to induce the alignment of LC molecules on a polyimide (PI) layer³⁻⁵. However, the rubbing method has some serious drawbacks resulting from the contact that arises in the rubbing technique, including the accumulation of electrostatic charge and the generation of fine dust⁶⁻⁸. For these reasons, alternative methods of LC alignment, based on non-contact processes, have been investigated to resolve the shortcomings of the PI-based rubbing method; these alternatives include the ultraviolet (UV) photoalignment technique⁶, nanoimprint lithography^{9,10}, oblique deposition¹¹, and ion-beam (IB) irradiation^{7,8,12-15}. Nevertheless, from an industrial point of view, these alignment methods are difficult to adopt at a commercial scale because of the surface treatments required for the substrates and the use of expensive vacuum equipment.

It was recently demonstrated that a preferred orientation of LC molecules can be achieved by adding nanomaterials to LCDs. Nakamura from Sharp developed a self-aligned LC-fullerene composite, wherein the surface can be vertically aligned without any LC alignment layers¹⁶. In addition, we have achieved the self-alignment of LC molecules by doping CuInS₂-ZnS-quantum dots¹⁷. Despite the simplicity of doping nanomaterials into LCs, additional processing for the nanomaterials is essential, with considerable cost.

Herein, we suggest a simple method for achieving the self-alignment of LC molecules by using nanocrystalline SnO₂ films deposited by a solution process. The solution process is simpler, has a higher throughput, allows easier composition modifications, and costs less than

vacuum deposition methods¹⁸. SnO₂, which has excellent dielectric properties and good optical characteristics, has already been evaluated for use as an LC alignment layer in previous studies^{12,13}. Uniform and homogeneous LC alignment was spontaneously achieved on nanocrystalline SnO₂ films. Moreover, we measured the alignment film properties and the electro-optical (EO) properties of electrically controlled birefringence (ECB) cells using various methodologies.

2. Experimental

ITO-glass substrates were subjected to several cleaning steps prior to the deposition process. The substrates were ultrasonically cleaned with acetone, methanol, and deionized water for 10 min each and then dried with N₂ gas. A 0.1 M SnO₂ solution was prepared for the alignment layer by mixing tin(II) chloride (SnCl₂) in 2-methoxyethanol (2ME). Mono-ethanolamine (MEA) and acetic acid were added dropwise for stability and homogeneity of the SnO₂ solution. Then, the solution was stirred at 75 °C for 2 hours using a hotplate magnetic stirrer and was aged at room temperature for at least 1 day. The SnO₂ solution was spin-coated onto the ITO-glass at 3000 rpm for 1 min. The SnO₂-coated substrates were then preheated at 100 °C for 10 min to remove any residual solvent. The resulting thin films were annealed at 100 °C, 200 °C, 300 °C, 400 °C, and 500 °C in a furnace for 1 hour.

The LC cells were fabricated with a pair of SnO₂ films mounted antiparallel to one another. A nematic LC (MJ001929, $n_e=1.5859$, $n_o=1.4872$, and $\Delta\epsilon=8.2$; Merck) was injected into the cells. The gap of the cell was 60 μm to allow for measurements of the pretilt angle and for polarized microscopy (BXP 51, Olympus) observations. A crystal rotation method (TBA 107, Autronic) was used to measure the pretilt angles of the LCs. The structural properties of the

SnO₂ films were characterized using X-ray diffraction (XRD) (DMAX-III A, Rigaku) and field-emission scanning electron microscopy (FESEM) (S-4200, Hitachi). The chemical bonding states of the SnO₂ were analyzed using X-ray photoelectron spectroscopy (XPS) (ES-CALAB 220i-XL, VG Scientific). ECB mode cells with a 2.5 μm cell gap were fabricated to verify the EO characteristics of the LC cells in an LCD application. The voltage-transmittance and response-time characteristics were measured with an LCD evaluation system (LCD-700, Otsuka Electronics).

3. Results and Discussion

The crystalline structure of the SnO₂ film deposited on the ITO-coated glass substrate was confirmed by XRD. As shown in Fig. 1(a), all of the diffraction peaks in the XRD pattern can be indexed to the rutile phase of SnO₂ (JCPDS No. 41-1445), and no impurities were observed for an annealing temperature of 500 °C. In contrast, an amorphous structure was observed for an annealing temperature of 100 °C owing to residual solvent. The average size of the SnO₂ nanocrystallinities for an annealing temperature of 500 °C, as deduced from Sherrer's formula for the strongest peak (110), was approximately 5.4 nm, which indicates that the solution-derived SnO₂ film was nanocrystalline.

To determine the mechanism of LC alignment, we performed physico-chemical analysis using XPS and FESEM because LC alignment is commonly affected by anisotropic alignment film properties that are determined by the chemical composition and by topographical changes in the film. The XPS spectra for the C 1s, Sn 3d, and O 1s peak were analyzed at the surface for various annealing temperatures, as shown in Fig. 2. All binding energies were referenced to the C 1s signal at 284.6 eV. As shown in Fig. 2(a), the peak for C-

O at 286.5 eV for the composition of the solvent decreased in inverse proportion to the annealing temperature¹⁹. This result indicates that the SnO₂ films were not fully formed at annealing temperatures below 300 °C owing to the presence of residual solvents. At annealing temperatures greater than 300 °C, the SnO₂ films were fully oxidized and gradually grew. Figure 2(b) shows XPS spectra for the Sn 3d_{5/2} and Sn 3d_{3/2} peaks. The binding energy of Sn 3d_{5/2} was centered at 486.5 eV for an annealing temperature of 500 °C, which corresponds to the fully oxidized value of Sn²⁰. The binding energy of Sn 3d_{5/2} shifted to a positive binding energy at annealing temperatures of less than 300 °C. This result arose from the coexistence of various Sn-O and Sn-Cl bonds in the SnCl₂-SnO₂ composite films because less oxidation occurred at annealing temperatures of less than 300 °C. We also observed a shift in the O 1s peak as a function of annealing temperature, as shown in Fig. 2(c). This result demonstrates that the SnO₂ films were gradually oxidized and grew as the annealing temperature increased.

Figure 3 shows FESEM images and UV-Vis transmittance spectra of the SnO₂ films deposited by solution processing onto ITO-coated glass substrates. The FESEM images show that the surface morphology of the SnO₂ films was strongly dependent on annealing temperature, as shown in Fig. 3(a)-(e). The nanocrystal sizes in the films clearly increased with increasing annealing temperature. However, the nanocrystal growth of the SnO₂ adversely affected the transmittance characteristics. As shown in Fig. 3(f), the average transmittance of the SnO₂ films over the wavelength range of 420-780 nm decreased from 84.52% to 81.21% with increasing annealing temperature. The decrease in transparency resulted from nanocrystal growth, which caused light scattering. However, the SnO₂ films exhibited transparencies similar to those of the as-prepared ITO glass and PI-coated ITO glass, which have transmittances of 83.23% and 83.52%, respectively, because the scattering

caused by the nanosized crystals of the SnO₂ films was fairly insignificant. Therefore, it can be concluded that SnO₂ films can be used as LC alignment layers with minimal loss of transparency.

To evaluate the LC alignment properties of the solution-derived SnO₂ films, LC cells with positive LC material were fabricated using various annealing temperatures. LC molecules can be uniformly aligned on the solution-derived SnO₂ films without imposing any external alignment processes under certain conditions. Photomicrographs of anti-parallel cells composed of SnO₂ films produced at various annealing temperatures are shown in Fig. 4(a). For annealing temperature below 300 °C, random alignment was observed. However, uniform and homogeneous LC alignment was observed for annealing temperature greater than 300 °C. This result can be clearly seen from the pretilt angle measurement. We measured the pretilt angles of the LC cells using the crystal rotation method. As shown in Fig. 4(b), the transmittance of each antiparallel LC cell was measured with a latitudinal rotation of $\pm 70^\circ$, and the oscillation of the transmittance was measured by LC cell rotation. The blue line depicts the simulated curve, while the red line shows the experimental curve. If the measured and simulated curves are identical, the LC alignment is uniform, and the pretilt angles of the LCs can be accurately estimated. The graphs of the measured pretilt angles indicate that the pretilt angles of the SnO₂ films can be determined with high reliability and that uniform LC alignment was achieved. The calculated pretilt angles of the LCs on the nanocrystalline SnO₂ films fabricated at annealing temperatures of 400 °C and 500 °C were 0.43° and 0.73°, respectively

As stated above, the use of nanocrystalline SnO₂ films can enable self-alignment of LC molecules. We conducted an additional experiment to investigate the effect of the nanocrystals of the solution-derived SnO₂ films. LCs were injected into the LC cells at room

temperature and at a temperature greater than the nematic-isotropic phase transition by using capillary force. Then, both LC cells showed clear statement. In addition, we observed random LC alignment on amorphous-phase SnO₂ films deposited by sputtering at a growth temperature of 50 °C in a previous study¹². These results indicate that the nanocrystalline SnO₂ films strongly influence a uniform alignment of LC molecules. The LC molecules on the nanocrystalline SnO₂ films were preferentially arranged along a filling direction when injecting LCs, and this arrangement was anchored via van der Waals forces by nanocrystals of SnO₂ films.¹⁷ The mechanism of the self-alignment of LC molecules on the nanocrystalline SnO₂ films is shown in Fig. 5.

The electro-optical properties of the LC cells were investigated in the ECB mode to examine the potential of the nanocrystalline SnO₂ films for LCD application. Figure 6(a) shows transmittance curves measured via the application of an AC voltage to the ECB cells fabricated with the nanocrystalline SnO₂ films. These ECB cells can be operated very simply compared to a conventional LCD using a PI alignment layer¹². The threshold voltages of the ECB cells composed of the nanocrystalline SnO₂ films fabricated at annealing temperatures of 400 °C and 500 °C were 1.657 V and 1.408 V, respectively. The threshold voltage defines an applied voltage at transmittance of 90%. Figure 6(b) shows the response-time curves of these ECB cells. The ECB cells composed of nanocrystalline SnO₂ films exhibited superior performance, with rise times of 1.55 ms and 0.73 ms and fall times of 2.97 ms and 2.45 ms, respectively. A short response time is important for reducing motion blur in LCD applications and color breakup in color-sequential LCDs. These enhanced results for ECB cells, combined with the self-alignment of the LC molecules, strongly support the use of solution-derived SnO₂ films with nanocrystalline structures.

4. Conclusions

In summary, we demonstrated the homogeneous self-alignment of LCs on solution-derived SnO₂ films with nanocrystalline structures. We confirmed the nanocrystallinity of SnO₂ films grown at temperatures greater than 400 °C through XRD and XPS analysis. Despite the increased nanocrystal grain size observed with increasing annealing temperature, the change in the average transmittance of the SnO₂ films as a function of annealing temperature was negligible. The self-alignment of LC molecules was achieved on the nanocrystalline SnO₂ films when these films were used as LC alignment layer, which is a valuable characteristic. Moreover, superior EO characteristics were observed for ECB cells fabricated from the nanocrystalline SnO₂ films, showing the remarkable potential of these films for LCD applications.

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Figure captions

Figure 1. XRD patterns of solution-derived SnO₂ films fabricated at annealing temperatures of 100 °C and 500 °C. All of the diffraction peaks in the XRD pattern corresponded to JCPDS file No. 41-1445.

Figure 2. XPS spectra of the (a) C 1s, (b) Sn 3d, and (c) O 1s core levels of solution-derived SnO₂ films fabricated at various annealing temperatures.

Figure 3. FESEM images of solution-derived SnO₂ film deposited on ITO-coated glass substrates at annealing temperatures of (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, and (e) 500 °C. (f) UV-Vis transmittance spectra of the solution-derived SnO₂ films.

Figure 4. (a) Photomicrographs of LC cells composed of solution-derived SnO₂ films fabricated at various annealing temperatures. "A" denotes "analyzer" and "P" denotes "polarizer". (b) Transmittance versus incident angle of the LCs on nanocrystalline SnO₂ films fabricated at annealing temperatures of 400 °C and 500 °C, as measured by the crystal rotation method to obtain the pretilt angle.

Figure 5. Mechanism of the self-alignment of LC molecules on nanocrystalline SnO₂ films. The LCs are oriented along the filling direction and align neighboring LCs via van der Waals interactions.

Figure 6. (a) Voltage-transmittance curve and (b) response-time curve of ECB cells fabricated with nanocrystalline SnO₂ films.

Figures

Figure 1.

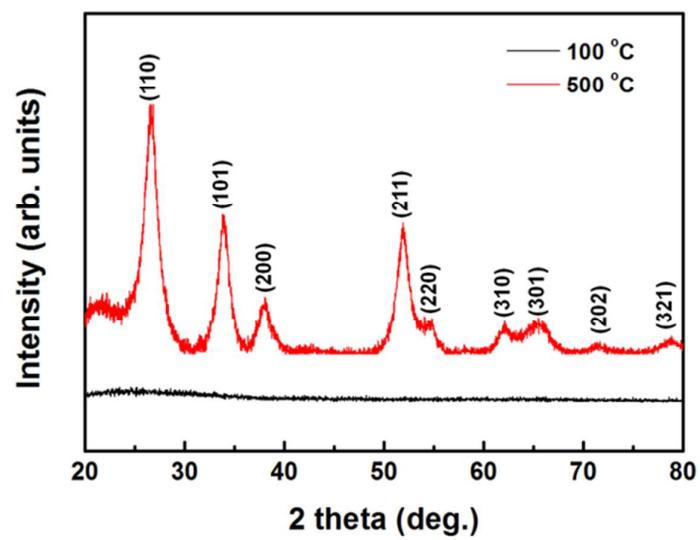


Figure 2.

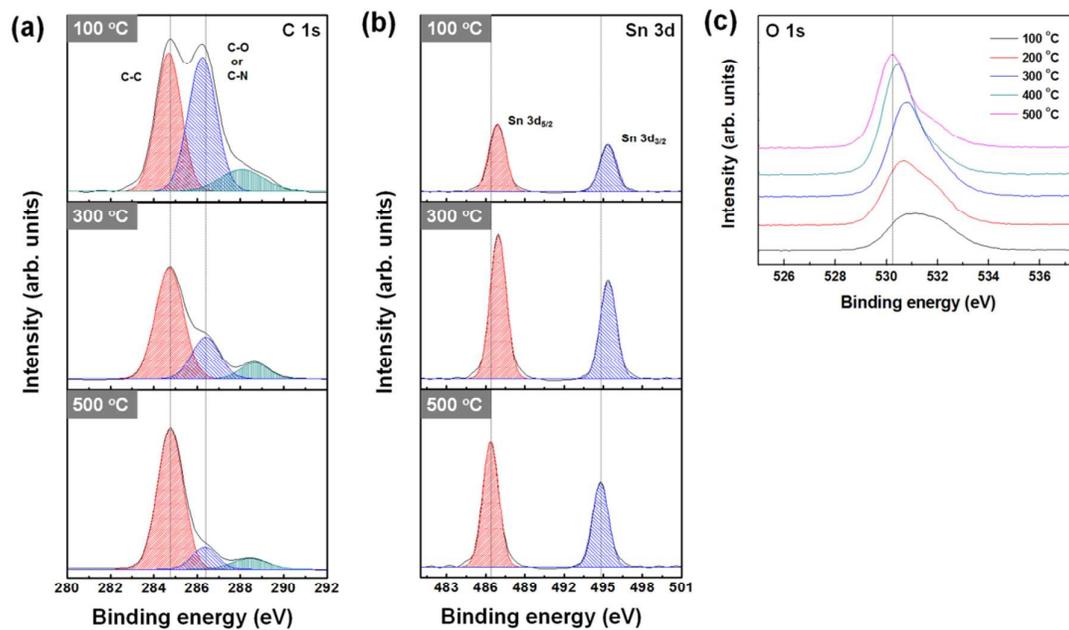


Figure 3.

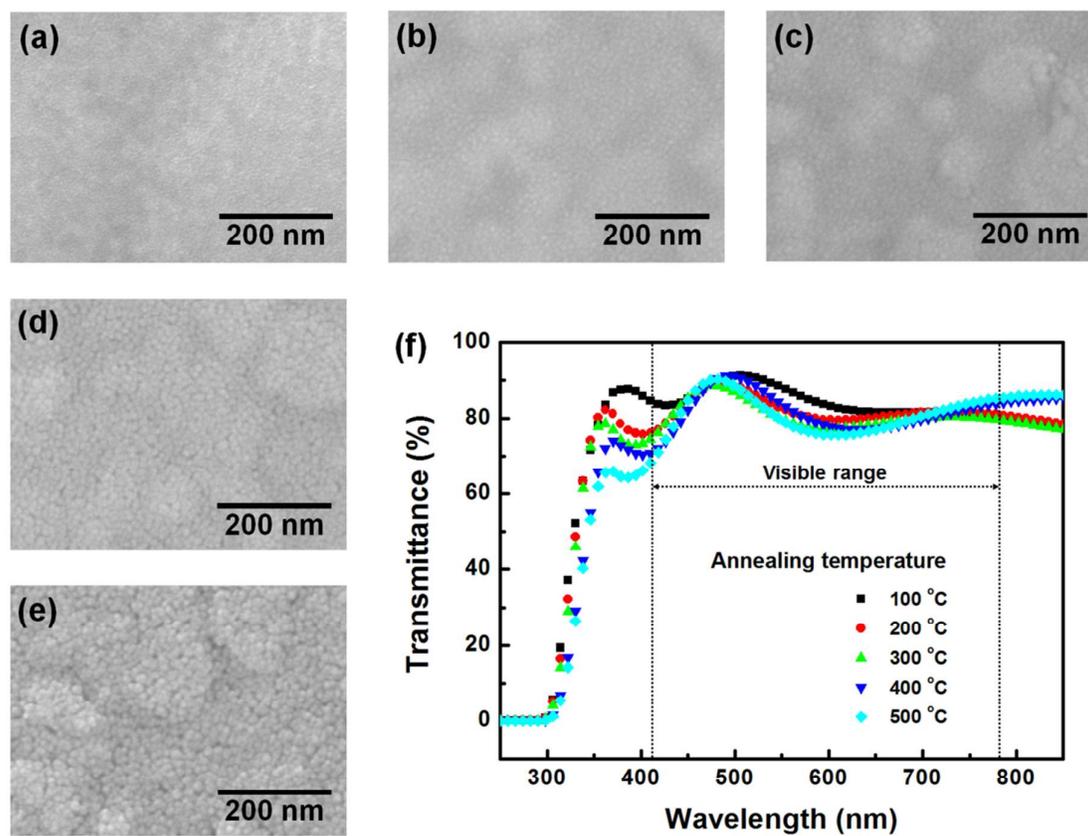


Figure 4.

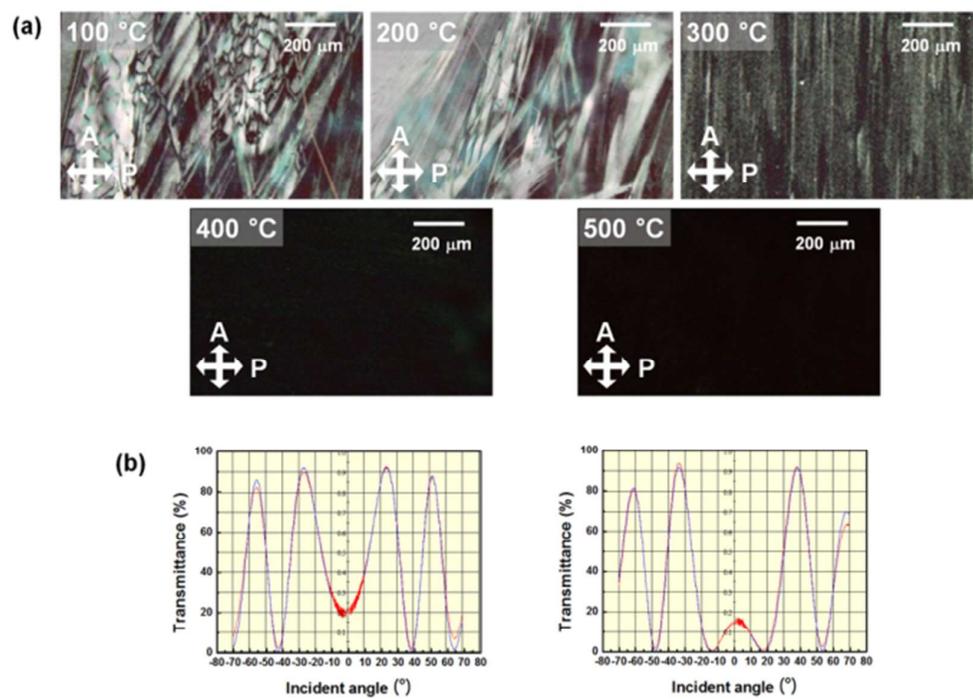


Figure 5.

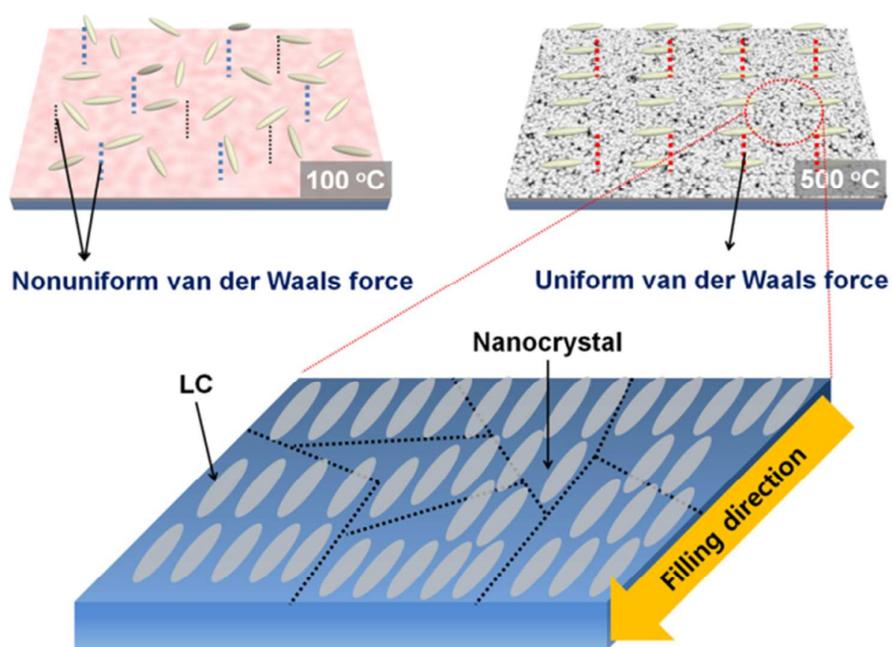


Figure 6.

