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Vertical alignment of liquid crystals with zinc oxide nanorods

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Abstract
The alignment of liquid crystals (LCs) on zinc oxide (ZnO) nanorods grown vertically on an indium tin oxide (ITO) layer has been investigated as an alternative alignment layer for the vertical alignment of LCs. We found that the degree of vertical alignment strongly depends on the length and density of the vertically aligned ZnO nanorods on the ITO layer and also that a uniform vertical alignment using the proposed structure can be achieved. Finally, vertically aligned LC cells with ZnO nanorods were fabricated and their electro-optical properties were evaluated and compared with those of a conventional vertically aligned LC cell with a polymer alignment layer.

(Some figures may appear in colour only in the online journal)

1. Introduction

In commercialized liquid crystal displays (LCDs), liquid crystals (LCs) are either vertically or homogeneously aligned. Representative wide-viewing-angle LC devices with homogeneous alignment are of the in-plane switching (IPS) [1, 2] mode and fringe-field switching (FFS) [3–5] mode, and in particular the latter dominate high resolution and high-end medium sized LCDs of less than 30″. Also, vertically aligned LC devices such as multi-domain vertical alignment (MVA) [6, 7], patterned vertical alignment (PVA) [8, 9], and polymer-stabilized vertical alignment [10–14] devices are widely used in large LC televisions because they show a high contrast ratio in normal directions and also do not require the rubbing process that is commonly used in IPS and FFS devices.

An alignment layer which shows strong anchoring of LCs in LCDs is absolutely required to achieve uniform orientation of LCs and to exhibit good reliability for the device. At present, most conventional vertical alignment LCDs use an organic polymer, a polyimide as an alignment layer, which requires coating and a baking process above 200 °C [15]. In general, an organic layer is relatively sensitive to heat and ultraviolet (UV) light so that the alignment characteristics might be damaged under long term exposure of heat and light sources with UV. In order to prevent such problems, in the case of displays for projectors, vertical alignment with a pretilt angle is achieved via a SiO oblique evaporation method [16, 17] because an inorganic alignment layer exhibits excellent stability under heat and UV. Recently, novel approaches to achieve vertical alignment of LCs using nanostructures such as a pillar-like structure with 2–3 μm pitch [18] and a nanoporous anodic aluminum oxide layer [19] were proposed. Both approaches show excellent vertical alignment though there seems to be some difficulty in fabricating nanostructures uniformly in large areas for practical purposes.

In this paper, we introduce vertically grown zinc oxide (ZnO) nanorods on an indium tin oxide (ITO) layer via a simple solution route [20] and test the alignment of LCs on the surface. ZnO is a wide band gap (∼3.37 eV) semiconductor having a high exciton binding energy (∼60 meV) which is 2.5 times higher than that of room temperature thermal energy [20, 21]. It is also known that ZnO is thermally stable to radiation resistance and is often utilized for antireflective coating layers on solar cells [22–25].

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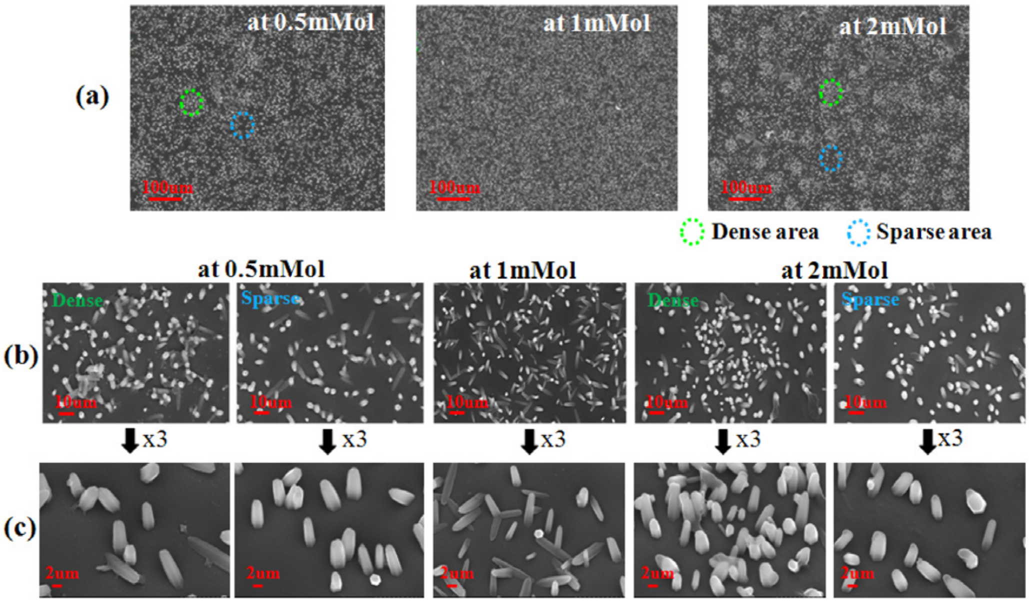

Figure 1. (a) Low magnification SEM images of ZnO nanorods grown on the ITO layer at 0.5, 1.0, and 2.0 mM $Zn(NO_3)_2$, (b) and (c) high magnification SEM images of ZnO nanorods in dense and sparse regions of (a), grown at different concentrations of $Zn(NO_3)_2$.

2. Experiment

We prepare three substrates at different concentrations of the mixture of zinc nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine ($C_6H_{12}N_4$) in water using a solution method in which ZnO nanorods are grown vertically on ITO coated glasses at 85 °C. Details of the growth of ZnO nanorods are available elsewhere [21, 26–28]. The length, diameter, and density of the ZnO nanorods can vary according to the concentration of each component in the mixture [26–28]. In particular, the surface morphology of ZnO nanorods on an ITO layer strongly depends on the molar concentration of $Zn(NO_3)_2$ in the mixture. In this work, molar concentrations of $Zn(NO_3)_2$ in water are varied from 0.5 to 2.0 mM, while keeping the concentration ratio of $Zn(NO_3)_2$ and $C_6H_{12}N_4$ at unity (i.e., 1:1). The ITO coated glass with grown ZnO nanorods and the other ITO coated glass with a conventional polymer type vertical alignment layer (AL60702, JSR.Co.) of thickness 100 nm are assembled together to give a cell gap of 9.4 μm. LC material (from Merck Advanced Technology) with a negative dielectric anisotropy ($\Delta\varepsilon = -4$ at 1 kHz) and birefringence ($\Delta n = 0.077$ at 589 nm) is used. The LCs are filled at room temperature by capillary force.

Figure 1 shows scanning electron microscopy (SEM) images of ZnO nanorods grown vertically on the ITO coated glass for the three cases. At a $Zn(NO_3)_2$ concentration of 0.5 mM, the ZnO nanorods have a mean length of 489 ± 124.96 nm and a mean diameter of 19.36 ± 2.8 nm. The density of the nanorods on average is 1.13 ± 0.25 μm^{-2} but a slight density difference between the areas is observed. When the concentration rate is increased to 1.0 mM, the ZnO nanorods are grown with a better uniformity and interestingly the nanorods are slightly tilted at random. The mean length and diameter of the nanorods are 561 ± 46.34 nm and 12.25 ± 1.8 nm, respectively. In comparison with a previous case, the density of the nanorods on average increases to 1.74 ± 0.10 μm^{-2} due to the increased concentration of $Zn(NO_3)_2$ which is used as a source of zinc. When the concentration of $Zn(NO_3)_2$ is further increased to 2.0 mM, the density of the grown ZnO nanorods has a non-uniformity from position to position and the mean diameter of the nanorods is about two times larger than that of the nanorods grown at 1.0 mM because the concentration of $Zn(NO_3)_2$ exceeds a reasonable proportion. The mean length, mean diameter, and density of the nanorods are 502 ± 117.64 nm, 24.1 ± 4.25 nm, and 1.62 ± 0.34 μm^{-2}, respectively. These results indicate that ZnO nanorods on ITO are most uniform in density when the concentration of $Zn(NO_3)_2$ is 1.0 mM.

3. Experimental results

Figure 2 shows the measured transmittance of substrates with ZnO nanorods grown on ITO coated glass for visible light (400–700 nm) using a LCD-1000S (Otsuka Electronics, Korea). The measured area is a circle with a diameter of 0.9 cm. An average transmittance is obtained by measuring six different points in a substrate area of 2.5 cm × 2 cm so that the transmittance here covers most of the substrates. Over a wavelength of 400–700 nm, the mean transmittance of the ITO coated glass with ZnO nanorods grown at 0.5, 1.0, and 2.0 mM $Zn(NO_3)_2$ is 67.6%, 68.3%, and 64.0%, respectively. In comparison, the mean transmittance of ITO coated glass is 88.3%. It is known that room temperature photoluminescence spectra from the ZnO nanorods grown by a solution method show a strong near band-edge ultraviolet emission at ~378 nm due to the recombination of free excitons through an exciton–exciton collision process, with a blue emission at 460 nm and a visible emission at 570–600 nm caused by intrinsic defects such as oxygen and zinc interstitials and oxygen vacancies [20, 21]. Hence, the

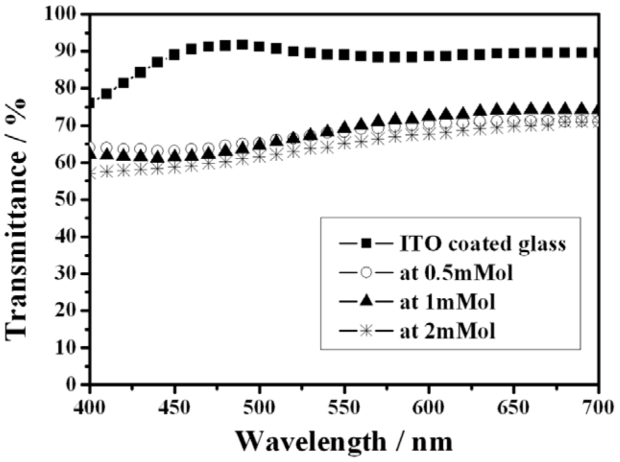

Figure 2. Measured transmittance of ZnO nanorods with different lengths and densities grown on ITO coated glass.

loss of transmittance in the range of 400–700 nm is attributed to light absorption by ZnO nanorods. It is also interesting to observe that the substrate with ZnO nanorods grown at 1.0 mM shows the highest transmittance, possibly due to greater uniformity in the light scattering compared to the cases of 0.5 and 2.0 mM, i.e., more of an antireflection effect induced by a higher density of ZnO nanorods at 1.0 mM than for the other cases.

The LC aligning characteristics have been tested by inserting the cell under crossed polarizers. As indicated in figure 3, the cells with nanorods grown at 0.5 and 2.0 mM $Zn(NO_3)_2$ do not show a dark state without a preferred optic axis, indicating the LC orientation is planar. Unlike these two cases, the cell with nanorods grown at 1.0 mM $Zn(NO_3)_2$ shows a clear dark state in most areas under normal observation because LC molecules are vertically aligned due to the uniform growth of the ZnO nanorods perpendicular to the substrate compared with those of the other two cases. Further vertical alignment is confirmed by conoscopic imaging and also light leakage in an oblique viewing direction, as shown in figure 3(b).

To reconfirm the vertical alignment of LCs by the alignment effect of ZnO nanorods, we grow nanorods only in defined areas using patterned ITO coated glass at 1.0 mM $Zn(NO_3)_2$ as shown in an optical microscopic image (see figure 4(a)). We then we fabricate a LC cell using the same procedure described above. Polarizing optical microscopic (POM) photographs of the fabricated cell show that a clear dark state is observed only in the areas with grown nanorods and the clear dark state is kept although the crossed polarizer is rotated as shown in figures 4(b)–(e), indicating that an excellent vertical alignment of LC molecules by ZnO nanorods is achieved.

For a comparison of the electro-optic properties with a conventional vertically aligned cell, we fabricate a vertical alignment cell with ZnO nanorods grown on whole ITO coated glass at 1 mM $Zn(NO_3)_2$. Figure 5 shows measured voltage-dependent normalized transmittance curves with insets of observed POM images of a dark and white state for both the proposed cell fabricated using the ZnO nanorods and a conventional cell fabricated using conventional polymer layers. The threshold and operating voltages of the conventional cell are 2.0 and 2.4 V, respectively whereas those

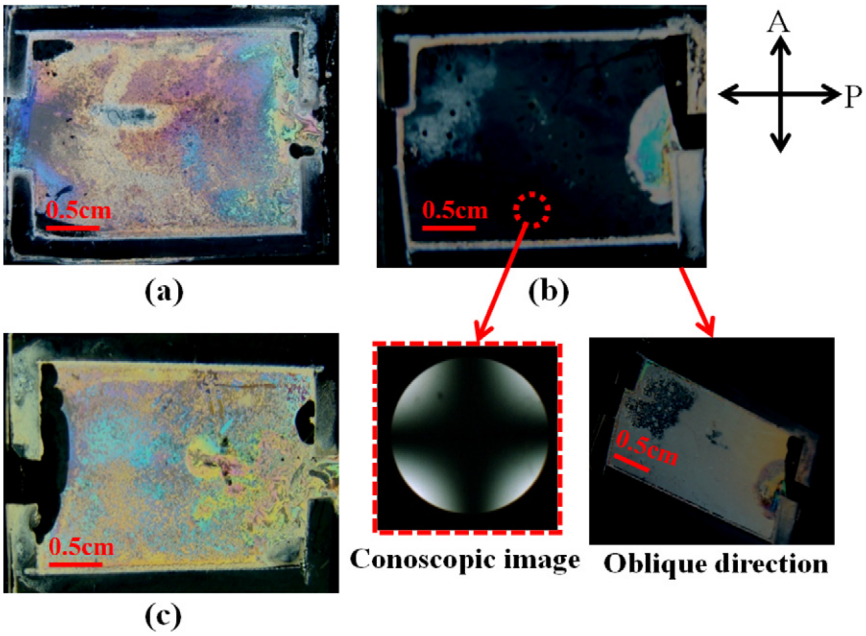

Figure 3. Macroscopic images of the fabricated LC cells using ZnO nanorods grown at (a) 0.5, (b) 1.0, and (c) 2.0 mM $Zn(NO_3)_2$ with crossed polarizers under normal observations. Additional photographs which show symmetric four-brushed texture under conoscopic observation of a dark area and light leakage in oblique viewing of the cell using ZnO nanorods grown at 1.0 mM $Zn(NO_3)_2$ confirm that the LCs are vertically aligned.

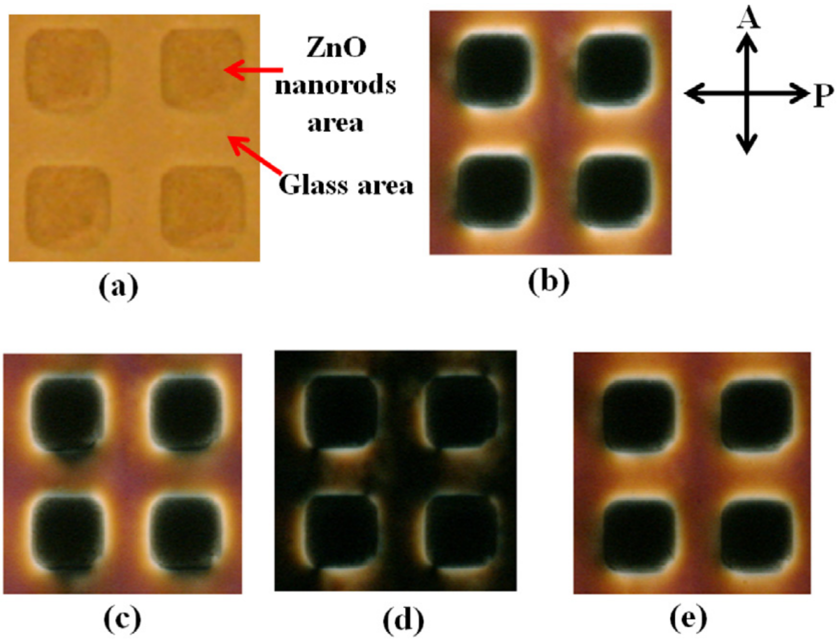

Figure 4. (a) Optical microscopic photograph of ZnO nanorods grown on patterned ITO coated glass and polarizing optical microscopic photographs of the cell with ZnO nanorods on patterned ITO coated glass while rotating the crossed polarizer: (b) 0°, (c) 30°, (d) 60°, and (e) 90°.

of the proposed vertically aligned cell are 1.9 and 2.2 V, respectively (see figure 5(a)), implying that the anchoring force of the nanorods is comparable to that of the polymer layer. POM images in a voltage-off state show an excellent dark state for both cells. Interestingly, POM images with the operating voltage show quite different textures for both cells. In the conventional vertically aligned cell, disclination lines with chevron textures exist due to collision between LC molecules in the voltage-on state because there is no preferred tilting direction at all. In the proposed vertically aligned cell, when the operating voltage is applied the disclination lines emanating from collisions between LC molecules appear instantaneously during the evolution of LC reorientation but disappear at a final stable state. As shown in figure 1(c), most of the ZnO nanorods grown at 1.0 mM $Zn(NO_3)_2$ are somewhat tilted. Hence, the disappearance of disclination lines at the operating voltage might be associated with tilted nanorods. In order to confirm whether the LC layer in the white state has an optic axis or not the crossed polarizer is rotated and the relative transmittance is measured using an *i*-solution image analyzer (*i*MTechnology). As indicated in figure 5(b), the cell shows maximal transmittance at a rotation angle of 80° and minimal transmittance at an angle of 40° and the angles which show maximal and minimal transmittance are repeated at every additional rotation angle of 90°, indicating that the LCs tilt down toward an azimuthal angle of on average 40°. However, a detailed observation of the LC texture at a rotation angle of 40° does not exhibit a complete extinction of the light, implying that the tilted angle is not uniform over whole surfaces. In order to find out whether there is any correlation between the tilted direction of the nanorods and the tilting direction of the LC director, we have investigated the tilted direction of each nanorod in detail using figure 1(b) at 1 mM. The number of nanorods tilted toward azimuthal angles of 40° and 130° were 44 while the rest, about 27, were in a given area of 14 544 μm^2 indicating a strong relationship between the tilted direction of the nanorods and the tilting direction of the LC director. Because of these structures, tilted nanorods in different directions cause competition between the elastic energies of LCs in each domain in the on state, allowing LC reorientation to prefer to align toward that azimuthal direction. It is known that the initial direction of growth is affected by the crystal orientation of the substrate surface (i.e., the grain orientation) [29]. It is worthwhile to note that as-grown ZnO nanorods have an n-type semiconducting property in nature [20, 30] thus the nanorods are likely to be tilted as the nanorod density increases because more repulsion at higher density is induced. Therefore, it is expected that the tilted angle could be controlled by controlling the nanorod density, for example, the tilted angle is more random at a low density but is tilted preferentially in a certain direction at a high density. However, to verify such a relationship, further study is needed in terms of the grain orientation and the electrical repulsion. Thus, it is expected that the tilted angle could be controlled by controlling the nanorod density. The reduction of threshold and operating voltages in the proposed cell are also related to the existence of a pretilt angle. Response times for both cells have been measured as well. Rising times (τ_r) for the conventional and proposed vertically aligned cells are 124 ms and 88 ms, respectively, which is a rather surprising result because τ_r is inversely proportional to the square of the applied voltage and the applied voltage in the proposed cell is 2.2 V while it is 2.4 V in the conventional cell. We believe the difference stems from whether there is a pretilt angle or not because the existence of a pretilt angle makes disclination

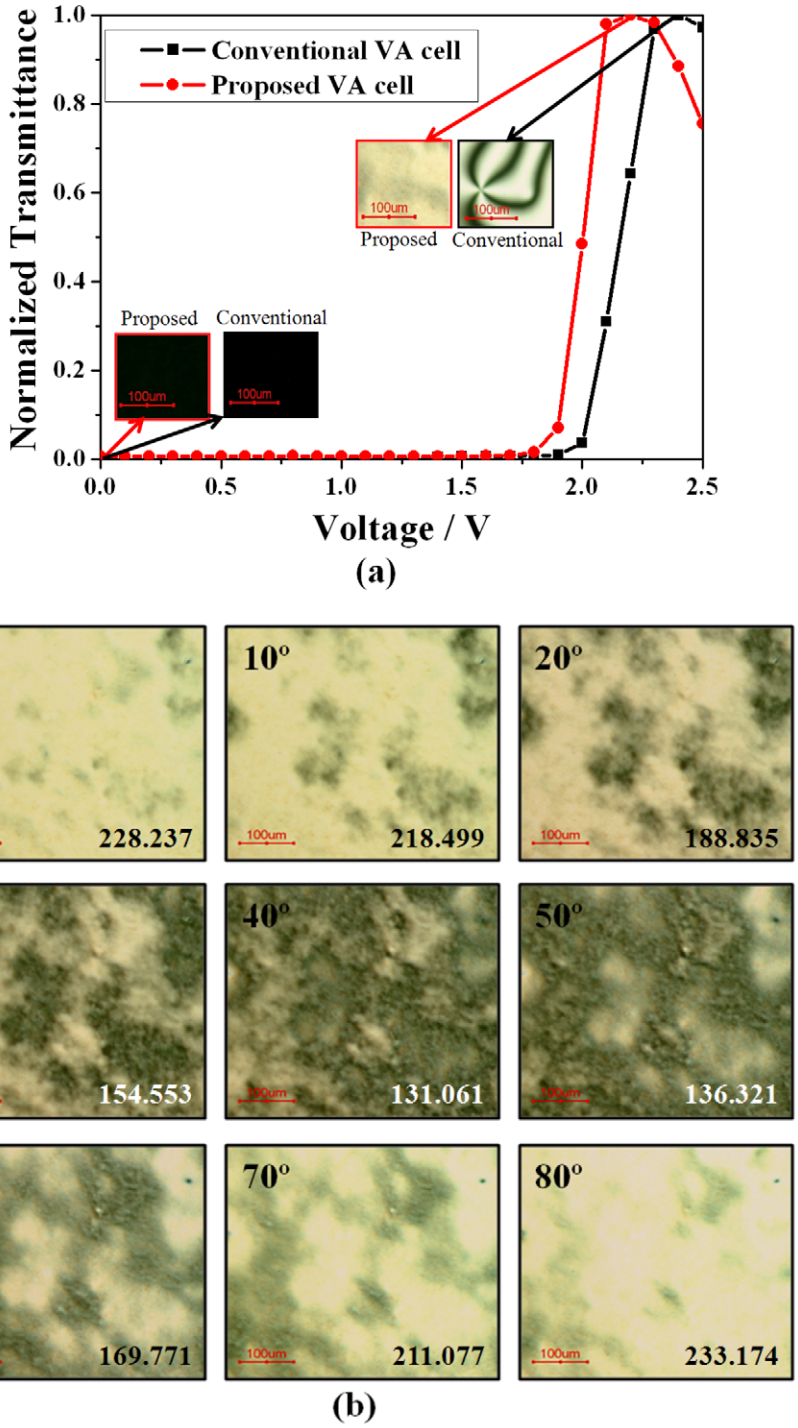

Figure 5. (a) Measured voltage-dependent normalized transmittance curves for the conventional and proposed vertically aligned cells. The insets are POM images in voltage-off (dark) and -on (white) states for the proposed cell and the conventional vertically aligned cells. (b) POM images of the proposed vertically aligned cell at operation voltage according to rotation of the crossed polarizers. Here the numbers inside the images indicate relative transmittance to each other.

lines disappear, i.e., the collision between LC molecules is minimal, allowing faster field induced reorientation of LCs. Decaying times (τ_d) for both cells show about the same level. In general, τ_d is proportional to the pretilt angle [31] such that if there is a 2° or 3° deviation from vertical alignment, τ_d will be slower than that for 90° vertical alignment. Therefore approximately the same value indirectly informs us that the preferred pretilt angle on average is close to 90° although individual nanorods are tilted.

4. Conclusion

In conclusion, we have introduced a new vertical alignment of LCs based on ZnO nanorods which are grown vertically on an ITO coated substrate using an electrochemical deposition method. The length and density of the ZnO nanorods strongly depend on the concentration of $Zn(NO_3)_2$ in water. The uniformly formed nanorods induce an excellent vertical alignment of LCs and the cell with the nanorods exhibits comparable electro-optic switching to that of a conventional vertically aligned cell based on a polymer layer.

Acknowledgments

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