Liquid crystal alignment on zinc oxide nanowire arrays for LCDs applications

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Abstract: The zinc oxide (ZnO) nanowire arrays on the indium tin oxide (ITO) glass substrates were fabricated by using the two-step hydrothermal method. A high transmittance ~92% of ZnO nanowire arrays on ITO substrate in the visible region was obtained. It was observed that the liquid crystal (LC) directors were aligned vertically to the (ZnO) nanowire arrays. The properties of ZnO nanowire arrays as vertical liquid crystal (LC) alignment layers and their applications for hybrid-aligned nematic LC modes were investigated in this work.

OCIS codes: (160.3710) Liquid crystals; (160.4236) Nanomaterials; (220.4241) Nanostructure fabrication; (230.3720) Liquid-crystal devices.

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#197536 - $15.00 USD Received 12 Sep 2013; revised 6 Nov 2013; accepted 6 Nov 2013; published 19 Nov 2013

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1. Introduction

Liquid crystal (LC) alignment is one of the important processes for fabricating liquid crystal devices (LCDs). It can provide LC molecules a specific orientation. The conventional alignment layer used for LCDs industry is the polyimide (PI) film. The synthesis of PIs in the LCD industry has been a mature technology [1]. However, there still have alternative alignment technologies developed to achieve LC alignment for different purposes, such as the photo alignment for obtaining contact-free process [2], polymer-stabilized alignment for improving electro-optical properties [3,4], and the polyhedral oligomeric silsesquioxanes (POSS) nanoparticle-induced vertical alignment for developing plastic LCDs requiring low temperature process [5,6]. Recently, several groups have investigated a new alignment technology by using inorganic nanoporous anodic aluminum oxide (np-AAO) films [7–9]. The np-AAO film can provide regular pores on the substrate, and the LC molecules result in a vertical alignment on the porous surface. The inorganic alignment films will be particularly promising for use in LC projector systems operated in a severe environment, where a highly reliable material is required.

Superior quality of the anisotropic ZnO nanostructure can be grown successfully via the various approaches, such as the metal organic chemical vapor deposition [10], thermal evaporation [11], and hydrothermal method [12–14]. Among of them, the solution-based hydrothermal method owns the advantages of low manufacture temperature and well-controlled nanostructure of variable size and shape on versatile substrates. Due to the excellent thermal stability and high transparency, the aligned ZnO nanomaterials have become the promising materials for a wide variety of photonic devices, such as field emitters [15] and solar cells [16]. Recently, a vertical alignment of LCs on ZnO nanorods grown by a solution route was reported by Lim *et al.* [17]. However, the grown ZnO nanorods with a density of ~1.7 μm^{-2} were slightly tilted randomly on the substrate and the transmittance of the ZnO nanorods/ITO substrate was low ~65% due to the light absorption and scattering of ZnO nanorods [17].

In this work, we synthesized the ZnO nanowire arrays by the hydrothermal method with the two-steps process. The ZnO seed layers were firstly prepared by deposition of zinc acetate and 2-(dimethylamino)ethanol mixture into thin film, followed by calcination. The ZnO nanowires were then grown on those seed layers from a bath solution comprising zinc sulfate and ammonium salt in water. The starting materials and growth temperature are different from previous studies in the literature [17]. The ZnO nanowire arrays were grown perpendicularly and uniformly with a density of 600μm-2 on the ITO glass substrate. The high transmittance ~92% of the ZnO nanowire arrays/ITO substrate was observed, which is extremely important for the LCDs applications. The characteristics of ZnO nanowire arrays as the vertical alignment layers and their applications for hybrid aligned nematic LCDs (HAN-LCDs) were investigated.

#197536 - $15.00 USD Received 12 Sep 2013; revised 6 Nov 2013; accepted 6 Nov 2013; published 19 Nov 2013

2. Experimental

All the chemicals used in this work were purchased from Alfa Aesar and used without further purification. The detailed preparation of ZnO nanowire arrays on ITO glass substrates is described as follows and the schematic illustration is shown in Fig. 1. A solution of zinc acetate dihydrate (0.82 g, 3.73 mmol) in 15 mL of isopropanol was stirred vigorously at 60°C for 10 minutes. 2-(Dimethylamino)ethanol (0.33 g, 3.75 mmol) was slowly added to the above solution and stirred at the same temperature for an additional 2 hours to form a homogeneous precursor solution. The solution was then cooled to room temperature and spin-cast into a thin film on the ITO glass substrate. The coated thin film was calcination at 200°C in air for 30 minutes to form ZnO seed layers. A bath solution consisting of zinc sulfate heptahydrate (0.29 g, 10 mmol) and ammonium chloride (2.14 g, 400 mmol) in 50 mL of de-ionized water was prepared. 2M NaOH aqueous solution was then slowly added for adjusting the *p*H value of the solution to 10 [16]. The ITO glass substrate with ZnO seed layers (ZnO/ITO substrate) was immersed in the above bath solution (ZnO seed layers downward) and placed in a preheated oven (60°C) for 45 minutes. The ZnO/ITO substrate was then washed with de-ionized water, acetone, and isopropanol, followed by calcination at 300°C in air for 30 minutes to form the final ZnO nanowire arrays [18]. The morphology of ZnO nanowire arrays was observed by using a field emission scanning electron microscope (SEM, Hitachi SU8000) The transmittance of ZnO nanowire arrays on ITO glass substrates (ZnO NW arrays/ITO substrate) was characterized by using an UV-visible spectrometer (Acton SP2150).

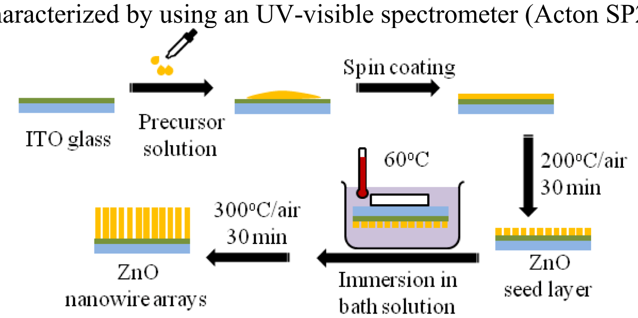

Fig. 1. The schematic illustration of fabrication process of the ZnO nanowire arrays on the ITO glass substrate.

To characterize the vertical alignment of ZnO nanowire arrays, the LC cells (namely VA-LCDs) containing a pair of ZnO NW arrays/ITO substrates were fabricated with a cell gap of ~6.5 μm as shown in Fig. 2(a). To demonstrate the application of ZnO NW arrays for the HAN-LCDs, HAN-LCDs with a rubbed homogeneous PI alignment layer and a ZnO NW arrays /ITO substrate were fabricated with a cell gap of ~7 μm as shown in Fig. 2(b). The LCs of negative dielectric anisotropy ($\Delta n = 0.085$, $\Delta\varepsilon = -4.1$) and positive dielectric anisotropy ($\Delta n = 0.23$, $\Delta\varepsilon = 14.5$) were filled into the VA-LCD and HAN-LCD by capillary action at room temperature, respectively. The polarizing optical microscope (POM) and the conoscopic measurement were used to investigate the LC alignment. The voltage-dependent transmittance of LC cells placed between crossed polarizers was measured using a diode laser (~637 nm), and the applied voltage was 1kHz square wave.

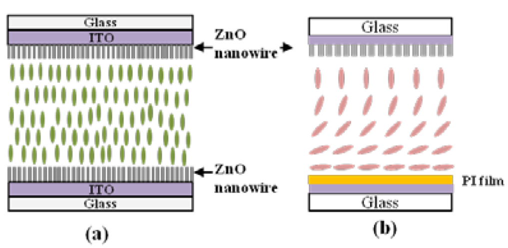

Fig. 2. The schematic illustration of the LC cells studied in this work. (a) VA-LCD, and (b) HAN-LCD.

#197536 - $15.00 USD Received 12 Sep 2013; revised 6 Nov 2013; accepted 6 Nov 2013; published 19 Nov 2013

3. Results and discussion

The nanostructure and the morphology of the ZnO NW arrays/ITO substrates observed by SEM were shown in Fig. 3. It can be seen that most of ZnO nanowire grew vertically on the substrate with diameters of 25-50 nm as shown in Fig. 3(a). The measured thickness of the seed layer is ~70 nm and the length of ZnO nanowire is ~200 nm as shown in Fig. 3(b). The density of ZnO nanowire arrays is 600μm^{-2} These geometric parameters are controllable, such as by changing the growth time and solution composition.

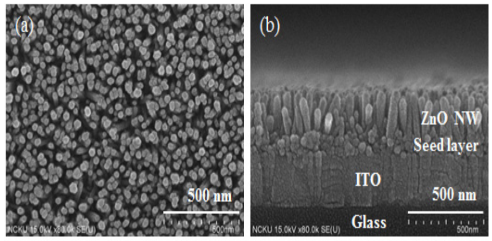

Fig. 3. The SEM images of ZnO NW arrays /ITO substrates. (a) Top view and (b) cross section view.

The UV–vis transmittance spectra of the ZnO NW arrays/ITO substrate and ITO glass substrate for three different incident angles were measured and compared as shown in Fig. 4. The transmittance of the ZnO NW/ITO substrate for light incidence perpendicular to the substrate is around 92% in the visible region, which is higher than the ITO glass substrate. The observed high transmittance of the ZnO NW arrays/ITO substrate is believed due to the antireflection effect of ZnO nanowire arrays. ZnO nanowire arrays with a broadband reflection suppression from 400 to 1200 nm has been reported and applied on solar cells [19,20]. The low transmittance ~65% of ZnO nanorods/ITO substrate observed by Lim *et al.* may be due to the non-uniform and sparse nanorods (density ~~1.7 μm^{-2}) [17], which cannot provide a structured film with the refractive index gradient for antireflection [19–21]. Lim *et al.* also claimed that the low transmittance was due to light absorption by ZnO nanorods [17]. The absorption of ZnO nanowire arrays strongly depends on the synthesis conditions [22], such as zinc source [23] and manufacturing temperature [24]. We believe that the differences in transmittance of ZnO NW arrays/ITO substrate between Lim *et al.* and ours are due to the different synthesis conditions and the density and uniformity of ZnO nanowire arrays. The properties of transmittance at large angles are important for LCDs. The transmittance of the ZnO NW/ITO substrate is higher than the ITO glass substrate for any incident angle due to the antireflection effect provided by the ZnO NW as shown in Fig. 4. The decrease in transmittance with the incident angle is mainly due to the increase of surface reflection at the interface of glass-air.

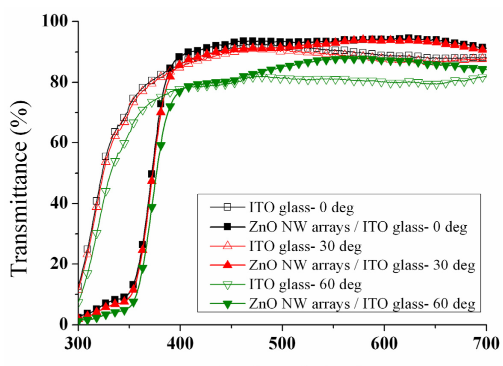

Fig. 4. The transmittance spectra of the ITO glass and ZnO NW arrays/ITO substrate at three different incident angles.

The photographs of VA-LCDs observed by POM with the crossed polarizers set in two different orientation with respective to the LC cells are shown in Fig. 5. The uniform dark state images indicate that LC molecules are aligned perpendicularly to the ZnO NW arrays/ITO substrate. In addition, the conoscopic images are also shown as the insets of Fig. 5. The typical connoscopic images of vertically aligned LCs are observed. For further confirmation of vertical alignment of LCs on ZnO nanowire arrays, we measured the pretilt angle of the VA-LCD by employing the crystal rotation method [25]. The pretilt angle is determined as 89.6°. It indicates that the whole LC molecules align almost vertically on ZnO nanowire arrays.

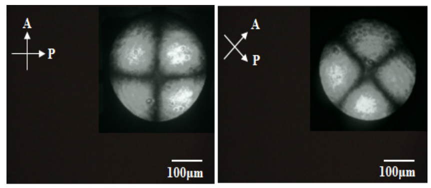

Fig. 5. Photographs of the VA-LCDs observed by POM with two different orientations of the crossed polarizers, where the insets illustrate the corresponding conoscopic images.

The voltage-dependent optical transmittance of the VA-LCD is shown in Fig. 6. The transmittance was normalized by the transmittance of parallel polarizers without the LC cell. The results show that the threshold voltage is around 2.2 V, which is close to the theoretical value [26]. The VA-LCD has a maximum transmittance of ~66% when applying 5.7 V. The low transmittance from the generation of disclination lines is due to the non-buffed ZnO nanowire alignment films as shown in the inset of Fig. 6. A uniform and tilted LC alignment on ZnO nanowire arrays may be achieved by growing ZnO nanowire arrays on an ITO glass substrate with asymmetric microgrooves. Maeda and Hiroshima have demonstrated that the np-AAO films on the ITO substrate with asymmetric microgrooves can obtain a disclination-free texture [8].

The HAN-LCD with a rubbed homogeneous PI alignment layer can also obtain a disclination-free texture. The voltage-dependent optical transmittance of the HAN-LCD is shown in Fig. 7. It has a maximum transmittance of ~85% when applying 1.7 V. The disclination-free texture is also shown in the inset of Fig. 7. The change of phase retardation for the proposed HAN-LCD from 0 V to 10 V is about 700 nm, which is greater than λ/2. Therefore, the voltage-dependent transmittance curve oscillates. We have also fabricated a traditional HAN-LCD with the homeotropic PI layer for comparison as shown in Fig. 7. They have similar features in the electro-optical properties as expected.

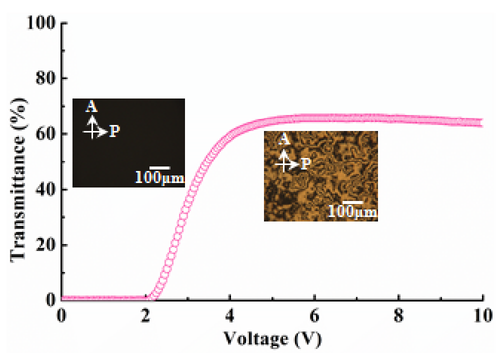

Fig. 6. The voltage-dependent optical transmittance of the VA-LCD. Two insets of a dark image and a bright image are observed by POM at $V = 0$ V and $V = 5.7$ V, respectively.

#197536 - $15.00 USD Received 12 Sep 2013; revised 6 Nov 2013; accepted 6 Nov 2013; published 19 Nov 2013

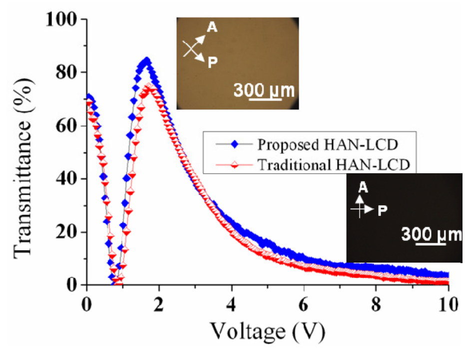

Fig. 7. The voltage-dependent optical transmittances of the proposed HAN-LCD and traditional HAN-LCD. Two insets of a dark image and a bright image are observed by POM at $V = 10$ V and $V = 1,7$ V, respectively.

4. Conclusions

The ZnO nanowire arrays were fabricated on ITO glass substrate by the two-step hydrothermal method, and their applications on vertical alignment of VA-LCDs and HAN-LCDs were investigated in this work. The transmittance spectra of ZnO NW arrays/ITO substrates showed a high transmittance ~92% and a colorless feature in the visible region. The electro-optical properties of VA-LCDs with ZnO NW arrays/ITO substrates revealed that LC molecules were vertically aligned with a pretilt angle of 89.6° on the ZnO nanowire arrays. The low transmittance ~66% in the bright state was obtained due to the non-buffed ZnO nanowire arrays. However, the transmittance of the HAN-LCD can reach ~85% by using one rubbed homogenous PI alignment layer. The study of influences of size and density of ZnO nanowire arrays on LC alignment is in progress.

Acknowledgments

The authors thank National Science Council of Taiwan for financially supporting this research under contract NSC 100-2112-M-009-014-MY3 and NSC100-2113-M-009-012-MY2.