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Tsung-Ta Tang^a, Chi-Yuan Hung^a, Ru-Pin Pan^a, Chitsung Hong^b & Weileun Fang^{b,c}

^a Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, R.O.C.

^b Institute of Nano-Engineering and Microsystems, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.

^c Department of Power Mechanical Engineering, National Tsing Hua University, Hsinchu, Taiwan, R.O.C.

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Vertical Alignment of Liquid Crystal on ITO Glass with Anodic Aluminum Oxide Thin Film

TSUNG-TA TANG,¹ CHI-YUAN HUNG,¹
RU-PIN PAN,¹ CHITSUNG HONG,² AND
WEILEUN FANG^{2,3}

¹Department of Electrophysics, National Chiao Tung University,
Hsinchu, Taiwan, R.O.C.

²Institute of Nano-Engineering and Microsystems, National Tsing Hua
University, Hsinchu, Taiwan, R.O.C.

³Department of Power Mechanical Engineering, National Tsing Hua
University, Hsinchu, Taiwan, R.O.C.

Anodic Aluminum Oxide (AAO) thin films have been demonstrated as a vertical alignment layer for nematic liquid crystal in recent years. To control the liquid crystal orientation by applying the electric field, the AAO alignment layers need to be fabricated on the transparent electrode. In this work, the liquid crystal cell with the AAO alignment layer on Indium Tin Oxide (ITO) transparent electrode has been demonstrated. The performance of the cell has been studied. The transmittance of AAO-ITO substrate is around 55%. The polar anchoring strength of the AAO-ITO cell with good vertical alignment is $1.32 \cdot 10^{-4} \text{ J/m}^2$, and the response time is around 90 ms.

Keywords Anodic aluminum oxide; ITO substrate; polar anchoring strength; response time; vertical alignment

1. Introduction

The liquid crystal displays (LCDs) are applied in many electrical productions, such as projectors, mobile phones, hand-held video game devices, and out-door advertisement applications, etc. One of the crucial compounds in the LCDs is the alignment layer which can make liquid crystal molecules orientate in the specific direction. The common alignment layers are the rubbing polyimide film [1], the ion-beam bombardment film [2], and the SiO_x oblique evaporation film [3]. There are several drawbacks of the previous alignment methods. For the rubbing method, the static electricity and the surface defects caused by the friction could damage the thin film transistors, and the organic alignment polymer is not stable. Therefore, the modern alignment method is necessary to be developed for improving the alignment performance.

Address correspondence to Ru-Pin Pan, Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan, R.O.C. Tel.: +886-3-5731989; Fax: +886-3-5725230; E-mail: rpchao@mail.nctu.edu.tw

The anodic aluminum oxide (AAO) is an inorganic and colorless material. It was widely used to be the templates of nano-material fabrication, including metals, semiconductors, organics and polymers [4–7]. In 1992, V. P. Parkhulik and V. I. Shershulsky showed the theoretical model of fabricating AAO film [8]. The fabrication methods of the porous AAO films have been studied by U. Gösele's groups [9,10]. If the aluminum film is anodized in different electrolytes, the non-porous or porous AAO thin film can be fabricated. The porous AAO film is fabricated in acidic ($\text{pH} < 6$) or alkaline ($\text{pH} > 10$) electrolyte, and the non-porous AAO film is fabricated in neutral electrolyte ($\text{pH} = 7 \sim 9$). According to the previous properties, the porous AAO film is an excellent candidate of the alignment layer for LCDs applications. Recently, the vertical alignment of liquid crystal on the porous AAO film has been reported [11,12]. The pore sizes and the polar anchoring strength of the porous AAO thin film can be modified by controlling the anodizing voltage. However, the transparent electrode, the indium tin oxide (ITO) thin film, would be etched during the anodizing process, and then the porous AAO film can not attach on the damaged ITO thin film. Therefore, the anodizing process can not work on the ITO glass substrate. The AAO liquid crystal cell without the electrode is only operated by applying the magnetic field.

In this work, an improved procedure has been developed to fabricate the porous AAO thin film on the ITO glass substrate. The O_2 plasma treatment is a kind of surface treatment in optical-electrical application to increase the carrier concentration [13] or change the work function [14] in the organic light emitting diode application. Here, the O_2 plasma treatment is used for cleaning the ITO glass substrate and enhancing the adhesive ability between the adhesion layer and the ITO layer. The liquid crystal cell with the AAO-ITO alignment layers has been demonstrated. It is more convenient to electrically operate the liquid crystal cell for LCDs application. Following, the improved method is described in detail in Section 2. The performances of the AAO-ITO liquid crystal cell are presented in Section 3.

2. The Improved AAO-ITO Fabrication Method

The display-graded ITO glass substrate (from Wintek co.) was cleaned and dried in the clean room. After cleaning, the ITO surface was treated by O_2 plasma with 100 W in 3 minutes to modify the surface property. By using the e-gun evaporator, the titanium (Ti) thin film (99.995%) with 10 nm thickness was evaporated as the adhesion layer. The aluminum (Al) thin film (99.999%) with 500 nm thickness was evaporated on top of the titanium film. This multi-layer substrate with Al/Ti/ITO thin film was the anode of the anodizing system.

The anodizing system is a home-made electrochemical trough, in which the Al/Ti/ITO substrate was connected to anode and a platinum plate was connected to cathode. The electrolyte was 3 wt% oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) aqueous solution, and the temperature of the electrolyte is maintained at $6.0 \pm 0.5^\circ\text{C}$. The anodizing area was 2 cm by 2 cm. The anodizing voltage was kept in constant voltage mode at 40 V. After anodizing process, The AAO-ITO substrate was etched by the mixture of chromic acid (1.5 wt% H_2CrO_4) and phosphoric acid (6 wt% H_3PO_4) at 60°C . By this etching process, the pore size of the porous AAO thin film can be widened. Then, the AAO-ITO substrate was cleaned and dried in the oven at 110°C for 30 minutes. Figure 1 shows the scheme of anodizing and pore widening processes.

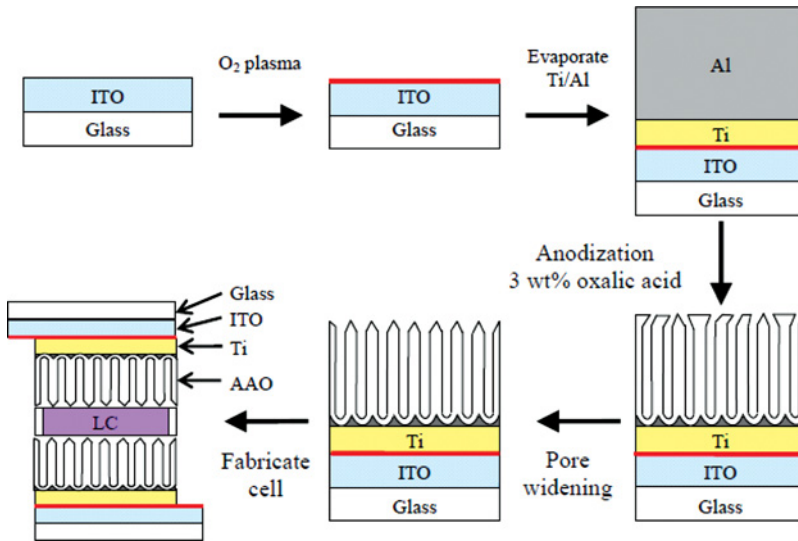


Figure 1. The scheme of the improved AAO-ITO fabrication method. (Figure appears in color online.)

After the AAO-ITO substrate was fabricated and cleaned, the transmittance of this substrate in visible region was investigated. By placing a pair of the AAO-ITO substrates face to face, the test liquid crystal cell was constructed. The performances of the test cell, such as the transmitted and the conoscopic images, the pretilt angle, the polar anchoring strength, and the electro-optical performance, were demonstrated, and the results were shown in the following section.

3. Results and Discussion

3.1. The Transmittance Spectrum in the Visible Region

The transmittance spectrum was taken by using a UV-Visible spectrometer (Oceanoptic, model ISS-UV-VIS and USB-2000) with air as reference. The dash line of Figure 2 shows the transmittance spectrums of the ITO substrate and the AAO-ITO substrate as functions of wavelength from 250 to 850 nm. The cut off wavelength at 350 nm is due to the absorption of glass substrates. According to Figure 2, the transmittance of the AAO-ITO substrate is around 60% in visible light range. It is comparable with the transmittance of the ITO substrate (solid line), around 80%. Although the transmittance of the AAO-ITO substrate is lower than the ITO substrate, the AAO-ITO substrates are acceptable for the LCDs applications.

3.2. The Alignment Properties of the Liquid Crystal Cell with the AAO-ITO Substrates

The liquid crystal cell is made a sandwich structure by putting the AAO-ITO substrates face to face. The mylar with 8.95 μm thickness is used as spacer. Because the AAO thin film is a vertical alignment layer, and the ITO electrode is parallel to the substrate. In order to control the liquid crystal molecules by the electric field,

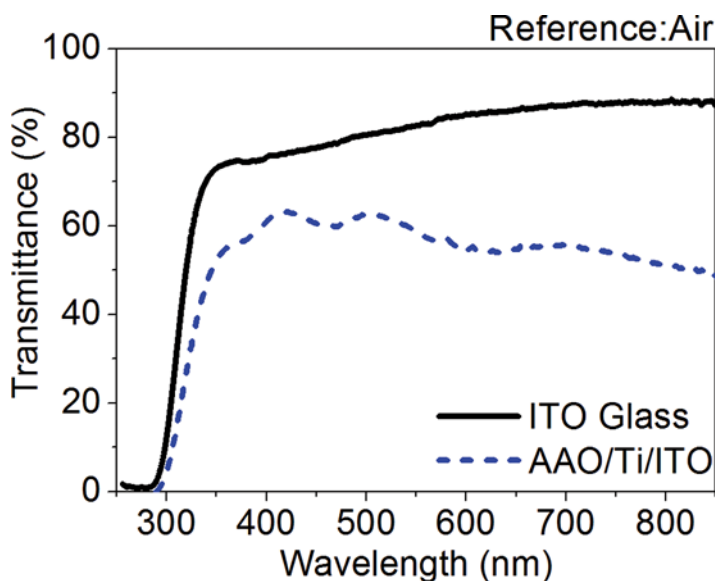


Figure 2. The transmittance of the AAO-ITO substrate (dash line) and ITO glass substrate (solid line). (Figure appears in color online.)

the liquid crystal with negative dielectric anisotropy, MLC-6608 (from Merck Co.), has been chosen to be filled into this cell. Furthermore, the AAO-ITO cell has been heat over the clearing point of MLC-6608 ($\sim 94^{\circ}\text{C}$) for 15 min. Figure 3(a) shows a conoscopic image of the AAO-ITO cell. The conoscopy is a method that can show the alignment and the tilt angle of the uniaxial crystal [15]. The conoscopic image of the homeotropical cell is a cross pattern which is corresponding to the Figure 3(a).

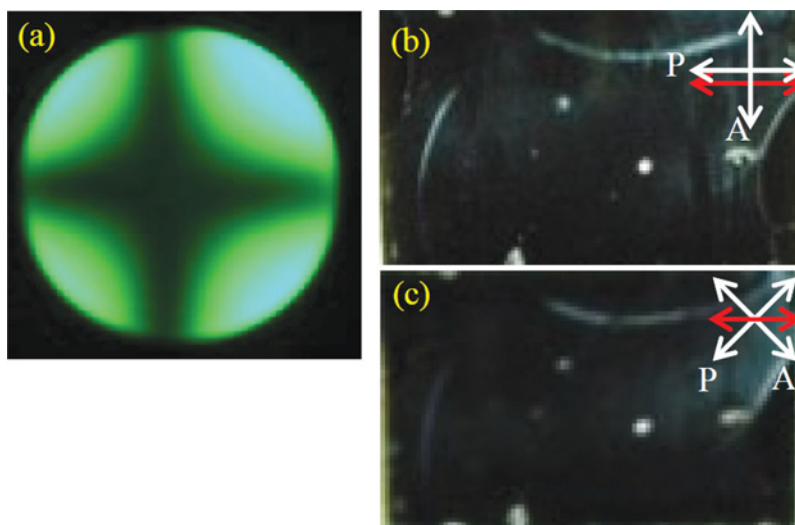


Figure 3. (a) The conoscopic image of the AAO-ITO cell; (b), (c) The transmitted images of the AAO-ITO cell in a pair of crossed polarizers. (Figure appears in color online.)

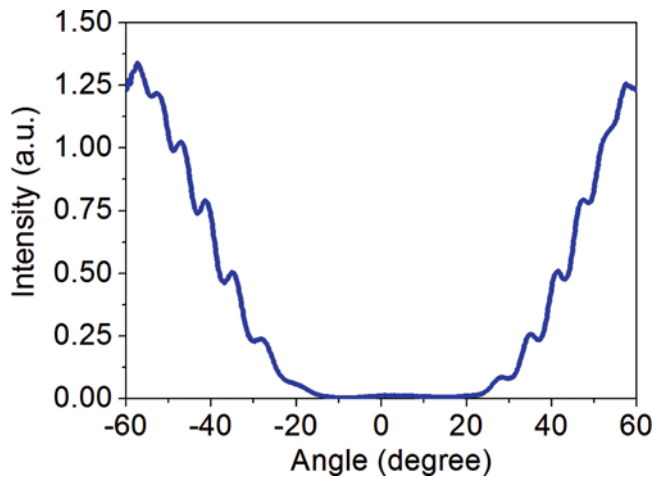


Figure 4. The transmittance of the AAO-ITO cell for pretilt angle experiment. (Figure appears in color online.)

It shows that the AAO-ITO thin film is a vertical alignment layer. Figure 3(b) and (c) show the transmitted images of the AAO-ITO cell which is placed between a pair of cross polarizers with two different orientations of the liquid crystal cell, 45° with respect to each other. Both of the images show the dark state, and it indicates that the AAO-ITO cell is a homeotropically aligned liquid crystal cell. According to Figure 3, the AAO film on the ITO electrode is still a good vertical alignment layer.

In addition, the actually pretilt angle is measured by using the crystal rotation method [16]. Figure 4 shows the measured data of the crystal rotation method with 632.8 nm at room temperature. In Figure 4, there are some symmetrical peaks which result from the interference of the liquid crystal layer. According to the constructive interference, the thickness of the liquid crystal layer is $9.00 \mu\text{m}$. Comparing to the cell gap without liquid crystals, there is a 0.7% deviation from that and it is too small to neglect the deviation. The pretilt angle the AAO-ITO cell is 89.5° . It shows that the AAO-ITO cell is a perfect vertical alignment cell.

3.3. The Polar Anchoring Strength

Another important parameter to quantify the vertical alignment ability is the polar anchoring strength. In the previous work [11], the polar anchoring strength of the porous AAO film with different pore sizes and different aspect ratio had been measured by applying the magnetic field [17]. In this work, the AAO thin film on ITO substrate has been fabricated successfully. The examined cell with the AAO-ITO alignment layer is exhibited as a vertical alignment cell, and the ITO transparent electrode still works well. Therefore, the polar anchoring strength can be measured by applying the electric field [18], instead of applying the magnetic field. The applied electric field would introduce a torque to rotate the liquid crystal molecules. For the liquid crystal with negative dielectric anisotropy, the liquid crystal molecules would like to rotate perpendicular to the electric field. By measuring the transmittance of the examined cell in a pair of crossed polarizers, the rotating angle of the liquid crystal molecules would be easily extracted, and the polar anchoring strength could be

calculated. In this measurement, the area of the electrode is necessary to be constant, 0.5 cm^2 , and the patterned ITO electrode was made by etching the ITO thin film before evaporating and anodizing Al thin film. The transmittance of the AAO-ITO cell was measured by changing the applying voltage, from $0.6\text{ V}_{\text{rms}}$ to $100\text{ V}_{\text{rms}}$, at room temperature ($\sim 25^\circ\text{C}$), and the wavelength of the incident light was 632.8 nm . The frequency of the applying voltage was 1 kHz . The polar anchoring strength of the AAO-ITO thin film is obtained as $1.3 \cdot 10^{-4}\text{ J/m}^2$, which is stronger than the polar anchoring strength of the common vertical alignment layer, N,N-dimethyl-N-octadecyl-3-aminopropyl-trimethoxysilyl chloride (DMOAP) as $7.1 \cdot 10^{-5}\text{ J/m}^2$ [19]. It means the AAO-ITO alignment layer is an excellent candidate for homeotropic alignment in LCDs applications.

3.4. The Voltage-Dependent Transmittance

The voltage-dependent transmittance was also measured at room temperature ($\sim 25^\circ\text{C}$), and the wavelength of the incident light is 632.8 nm . Figure 5 shows the transmittance of the AAO-ITO cell with different applying voltage. According to Figure 5, the transmittance is increased when the applying voltage is over the threshold voltage. The maximum transmittance is 27.6% at $5.5\text{ V}_{\text{rms}}$. Because the transmittance of a AAO-ITO substrate is around 55% , shown in Figure 2, the maximum transmittance of the AAO-ITO cell with two AAO-ITO substrate is theoretically around 30% . Therefore, the maximum transmittance of the AAO-ITO cell in Figure 5 is around 27.5% , which is less than 30% . The contract ratio is around $345:1$. These electrical performances indicate that the AAO-ITO cell can be operated by applying the electrical field. The electrical controllable cell was successfully demonstrated.

According to the relationship between the transmittance and the phase retardation, the voltage-dependent transmittance can be transformed into the voltage-dependent phase retardation, shown in Figure 6. By using the voltage-dependent

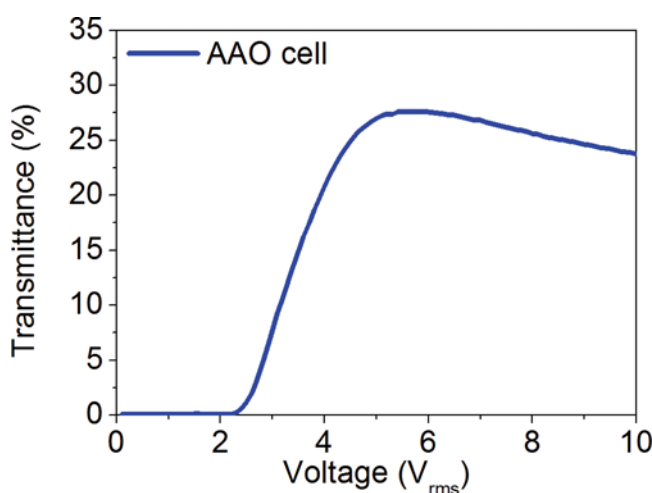


Figure 5. The voltage-dependent transmittance of the AAO-ITO cell. (Figure appears in color online.)

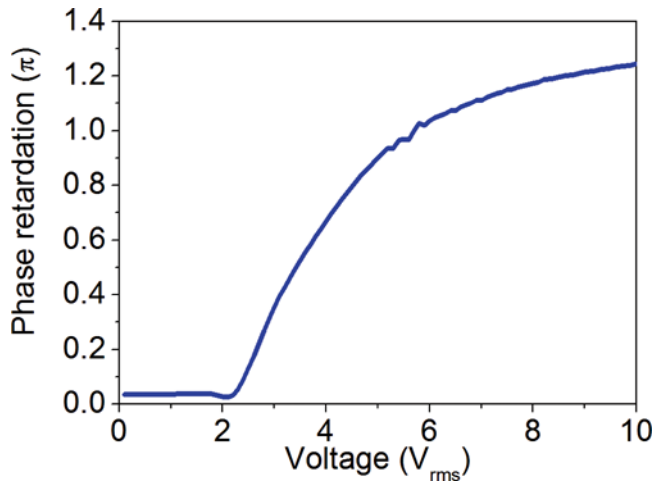


Figure 6. The voltage-dependent phase retardation of the AAO-ITO cell. (Figure appears in color online.)

phase retardation curve, the experimental threshold voltage of the AAO-ITO cell is decided as $2.2 V_{\text{rms}}$. It is well consistent with the theoretical threshold voltage which is $2.19 V_{\text{rms}}$. Therefore, the porous AAO thin films do not affect the electrical field to increase the threshold voltage. On the other hand, the operating voltage of the AAO-ITO cell is normal as the common liquid crystal cell and it is useful for LCDs applications.

3.5. The Response Time Measurement

The response time is also a very important performance of the LCDs applications. It indicates that how fast the liquid crystal molecules orientate from the bright state to

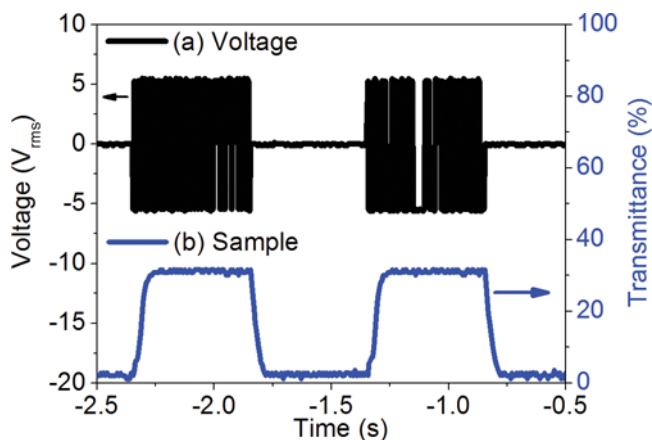


Figure 7. (a) The waveform of the applied voltage; (b) The transmittance of the AAO-ITO cell with the amplitude-modulated voltage for the response time measurement. (Figure appears in color online.)

the dark state. According to Section 3.4, the condition of the applying voltage at the maximum transmittance was chosen to measure the response time. The amplitude-modulated voltage was applied on the AAO-ITO cell. The amplitude of the voltage is $5.5 V_{\text{rms}}$ at 1 kHz, and the modulated frequency is 1 Hz. The waveform of the applied voltage is shown in Figure 7(a). Figure 7(b) shows the transmittance of the AAO-ITO cell with the amplitude-modulated voltage. By analyzing the transmittance, changed from 10% to 90% and from 90% to 10%, the rise time and the fall time can be easily determined, respectively. The rise time and the fall time of the AAO-ITO cell were measured in 47.8 ms and 43.0 ms, respectively. The theoretical fall time is 41.6 ms, which is corresponding to the experimental one. The rise time depends on the applying voltage. The larger voltage will give the fast response time.

4. Conclusions

The improved fabrication method of the porous AAO thin film on ITO electrode had been demonstrated in this work. The transmittance of the AAO-ITO substrate is around 55%. The nematic liquid crystal molecules can be aligned vertically on the AAO thin film with the ITO electrode. The transmitted and conoscopic images had been observed by putting the cell in a pair of cross polarizers. The electrical performance of the AAO-ITO cell had been determined. The polar anchoring strength of the AAO-ITO thin film is $1.3 \cdot 10^{-4} \text{ J/m}^2$ which is a good vertical alignment layer for LCDs application. The contract ratio is 345:1. The measured response time is around 90 ms. Further research has been processed to improve the performance of the electrical properties such as the response time and the contract ratio.

Acknowledgment

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