# Controlling the alignment of liquid crystals by nanoparticle-doped and UV-treated polyimide alignment films

Shie-Chang Jeng<sup>1,\*</sup>, Su-June Hwang<sup>2</sup>, Tai-An Chen<sup>1</sup>, Han-Shiang Liu<sup>3</sup>, and Mu-Zhe Chen<sup>1</sup> Institute of Imaging and Biomedical Photonics, National Chiao Tung University, Tainan 711, Taiwan

<sup>2</sup>Dep. of Electro-Optical Engineering, National United University, Miao-Li 360, Taiwan <sup>3</sup>Institute of Photonics System, National Chiao Tung University, Tainan 711, Taiwan

#### **ABSTRACT**

We have developed two approaches for controlling the pretilt angles of liquid crystal molecules by using conventional polyimide (PI) alignment materials either doping homogeneous PIs with Polyhedral Oligomeric Silsequioxanes (POSS) nanoparticles or treating homeotropic PIs with ultraviolet light. These techniques are very simple and are compatible with current methods familiar in the LCD industry. The characteristics of modified PI alignment films and their applications for photonic devices are demonstrated in this paper.

**Keywords:** liquid crystal devices, pretilt angle, polyimide, nanoparticle, UV-treatment

# 1. INTRODUCTION

The pretilt angle of a conventional liquid crystal (LC) device is either near zero degrees or 90 degrees for using commercial homogeneous and homeotropic polyimide (PI) materials, respectively. The control of the pretilt angle is very important to obtain a defect-free LC alignment and also to improve LCD performance, such as response time and viewing angle. The technique of producing homogeneous and homeotropic surface alignment is mature in the LC display (LCD) industry. However, the required pretilt angle of LCDs depends on the operation mode, e.g. near zero degrees for in-plane switching, several degrees for the twisted nematic mode, more than 5° for the supertwisted nematic mode, 45°-60° for no-bias optically-compensated bend (OCB) LCD and the bi-stable bend-splay (BBS) LCD [1-2], and near 90 degrees for the vertical alignment mode. There are many methods have been developed to control the pretilt angle of LC with a wide range, such as: SiOx oblique evaporation [3,4], polymer-stabilized alignment [5], nanostructured surfaces [6-8], hybrid mixture of two materials [9-11], chemical synthesis [12,13], and stacked alignment layers [14]. However, the mass production capability and ease of material synthesis for those developed techniques are questionable.

Recently, we have reported a new approach to align LC vertically by adding polyhedral oligomeric silsesquioxane (POSS) nanoparticles in LCDs [15,16]. The technique was applied to generate variable liquid crystal pretilt angles based on doping different concentrations of POSS nanoparticles in the planar-aligned LC layer [17]. The competition between the nanoparticle-induced vertical alignment and the horizontally aligned polyimide (PI) will result in the LC molecules realigning themselves to achieve a variable pretilt angle near the PI surface. However, it is not easy to reach a uniform distribution of POSS nanoparticles in the LC layer and to avoid POSS aggregation in the LC layer, therefore some scattering is produced around the POSS clusters and these reduce the contrast of LCDs.

In our recent work, we proposed and demonstrated a novel method that the pretilt angle of liquid crystal molecules can be continuously controlled by using conventional homogeneous PI alignment material doped with different concentrations of POSS nanoparticles [18]. The addition of POSS in the homogeneous PI lowers the surface energy of the alignment layer and generates the variable pretilt angle  $\theta_p$  in a range of  $0^{\circ} < \theta_p < 90^{\circ}$ . This method utilizes the conventional PI alignment materials, the manufacture processes and facilities, therefore it can readily be adopted by the current LCD industry.

\*scjeng@faculty.nctu.edu.tw

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It was also observed that the pretilt angle of an alignment layer can be controlled by UV irradiation [19-22]. UV irradiation on PI alignment films can induce extensive physical and chemical modifications for PI with or without photofunctional groups, such as photo-isomerization, photo-dimerization and photo-decomposition [21,22]. Techniques of photo-alignment by polarized or non-polarized UV had been intensively investigated in the 90s and have recently matured to practical methods for producing large LCDs [23]. UV-treated PI films have also been applied to fabricate LC devices, such as single-cell-gap transflective LCDs and LC Fresnel lens (LCFL) recently [24,25]. The desired pretilt angle can be achieved by using UV irradiation for controlling the surface energy of a PI film. Therefore, LC devices require patterned alignment areas with different pretilt angles can be obtained by this method.

In this paper, we reported two approaches for controlling the pretilt angles of liquid crystal molecules by using conventional PI material either doping homogeneous PI with POSS nanoparticles or treating homeotropic PI with UV. The surface energy of POSS/PI and UV-treated PI alignment layers were studied to investigate the mechanism of pretilt control. The LC devices, such as Fresnel lens and LC phase grating were fabricated and presented in this paper.

# 2. SAMPLE PREPARATION

# 2.1 POSS doped polyimide and UV-treated polyimide

In this experiment, we used an ultrasonic processor (S4000, Misonix) to produce the mixture of the POSS/homogenous alignment PI. The mixture of 0.2 wt% POSS was filtered through a 200 nm syringe filter. The mixture was then diluted with PI to generate different concentration of POSS in PI from 0.01 wt% to 0.07 wt%. The POSS/PI mixture was spin-coated on the ITO glass substrates to obtain a thin alignment film and then it was prebaked for 10 minutes and post-baked at 180°C for 4 hours to cure the POSS/PI mixture for forming the alignment layer. The surface of the alignment layer was subjected to rubbing treatment using a nylon cloth in such a way that the alignment was rubbed once in each direction.

To fabricate the UV-treated alignment layer, the buffed homeotropic PI layer, serving as LC vertical alignment layers, were first spin-coated on the two ITO substrates and then pre-baked at 100°C on the hot plate; finally, they were baked in a thermal oven for one hour. Subsequently, a UV light (intensity: 34.1 mW/cm2) illuminated the homeotropic PI film through a designed mask. After finishing UV illumination, the homeotropic PI film became horizontally aligned. The pretilt can be controlled by the UV exposure time and intensity.

The surface energy of the alignment film was determined by measuring the contact angle of distilled water on the film according to the Girifalco-Good-Fowkes-Young model [26]. To determine the pretilt angle and the polar anchoring energy (PAE) of LC molecules on UV-treated PI alignment layers, anti-parallel LC test cells were fabricated with a cell gap of 6.7 µm and were capillary filled with positive dielectric anisotropic LC molecules (E7). Pretilt angles of the LC cells were measured by the modified crystal rotation method [27,28].

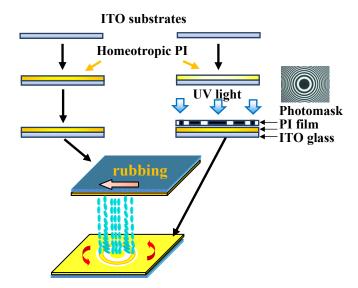
## 2.2 LC devices fabrication

#### 2.2.1. Fresnel LC Lens

A binary liquid crystal Fresnel lens (LCFL) can be easily fabricated by the UV-induced changes in the pretilt angle of the homeotropic PI films as shown in Fig. 1. An alternating pattern of hybrid-aligned and vertically-aligned LC cells was obtained by UV irradiation (intensity I  $\sim$  37 mW/cm<sup>2</sup>) of a homeotropic PI film through a photo mask with Fresnel zone patterns. Following UV irradiation, the homeotropic PI was modified to become horizontally aligned in the even zone areas. The design of the photo mask can be found in our previous work [25]. This photo-mask was designed to have a primary focal length  $f \sim 25$ cm at  $\lambda = 632.8$  nm.

As shown in Fig. 1, a polarization-independent LCFL can be obtained by the circular and horizontal buffing the UV-treated and the homeotropic PI films, respectively. Both buffed top and bottom substrates were then assembled into an LC cell with a cell gap of  $\sim$ 10  $\mu$ m maintained by spacers. The positive LC material (E7) was then injected into the empty cell.

To characterize the focus properties of the LCFL, the image quality and voltage-dependent diffraction efficiency were measured. As shown in Fig. 2, a He-Ne laser was magnified with a beam expander to approximately 1 cm in diameter corresponding to the active area of the LCFL. The polarization direction of the incident light with respect to the parallel buffing direction of the LCFL was controlled by a linear polarizer and a half wave plate. The focus properties of the LCFL can be measured by using a CCD camera and a photo detector, set ~25 cm from the LCFL.



Horizontal rubbing: polarization-dependent LCFL Circular rubbing: polarization-independent LCFL

Figure 1. The fabrication process of the liquid crystal Fresnel lenses.

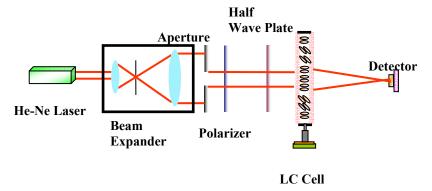


Figure 2. The experimental setup for measuring the focus properties of the LC Fresnel lens.

# 2.2.2. Phase grating

The homeotropic PI were spin-coated on the two indium tin oxide glass substrates, then pre-baked at  $90^{\circ}$ C on the hot plate for 10 min, finally they were baked at  $220^{\circ}$ C in a vacuum oven for 2 hours. Subsequently, the top and bottom substrates were assembled into a cell separated by  $5.5\mu m$  spacers such that the rubbing directions at the ITO glass plates were anti-parallel as shown in Fig. 3. The sample is then irradiated by UV through a grating photomask with the spacing around  $200 \ \mu m$ .

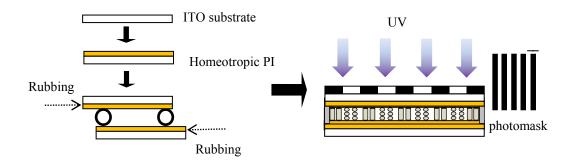


Figure 3. The fabrication process of the liquid crystal phase grating.

# 3. RESULTS and DISCUSSION

The results of the surface energy of the PI/POSS alignment layer with different POSS wt% doped in PI and the UV-treated PI with different irradiation are shown in Fig 4 and Fig. 5, respectively. It indicates that the addition of the POSS nanoparticles in the homogeneous PI mediates and lowers the surface tension of the alignment layer. However, the treatment of UV on homeotropic PI mediates and increases the surface tension. The pretilt angle of the rubbed PI film is observed to continuously decrease with increasing surface tension as shown in Fig. 4 and Fig. 5 for POSS/PI and UV-treated PI alignment layers, respectively. The influence of surface energy of alignment layer on pretilt angle has been investigated [28–30]. It showed that an alignment layer with higher surface energy gives the lower pretilt angle due to the increased attractive strength between LC molecules and molecules of the alignment surface.

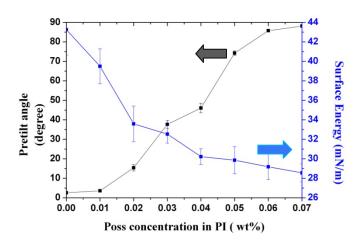


Figure 4. Pretilt angle and surface energy of POSS/PI alignment layers as a function of POSS concentration in PI.

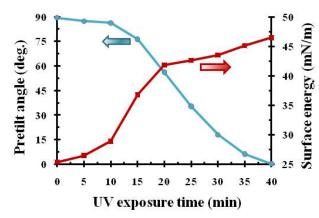


Figure 5. Pretilt angle and surface energy of UV-treated PI films as a function of intensity of UV exposure time, where the UV intensity was set at 37 mW/cm<sup>2</sup>.

The measured diffraction efficiency of a typical polarization-dependent LCFL as a function of the applied voltage is shown in Fig. 6. The diffraction efficiency progressively increases to the maximum diffraction efficiency  $\sim 35\%$  at V =1.1 V. In order to characterize the relationship between the imaging and focusing qualities of the LCFL, a black piece of cardboard with a transparent letter "U" was placed in front of the LCFL. The focusing images shown in Fig. 7 were recorded as the CCD camera located at positions, 20, 25, and 30 cm behind the LCFL. The inverted real image suggests that the LCFL reported here acts as a convex lens.

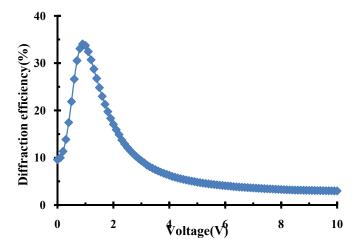


Figure 6. The voltage-dependent diffraction efficiency of a polarization-dependent LC Fresnel lens.

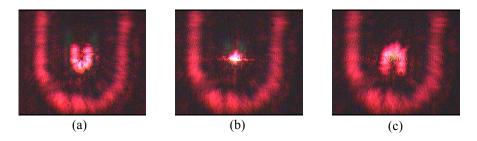


Figure 7. Images of the LC Fresnel lens recorded by a CCD camera. (a) before focal point 5cm, (b) at focal point, (c) after focal point, where the driving voltage is 1.1 V.

The images of the proposed LC phase grating observed by a crossed polarizing optical microscope (POM) are shown in Fig. 8. The dark regions where the PIs were not treated by UV are the LC with vertical alignment, and the bright regions where the PIs were treated by UV are LC with planar alignment. The first-order diffraction efficiency of the proposed LC phase grating as a function of the applied voltage is shown in Fig. 9. The first-order diffraction efficiency of a phase grating is determined by the relative phase difference between the UV-treated and the non UV-treated regions. If the direction of polarization is parallel to the grating, the phase grating has maximum diffraction efficiency. The diffraction efficiency decreases gradually to zero as the voltage increases, because all of the LC directors are reoriented almost perpendicular to the substrates.

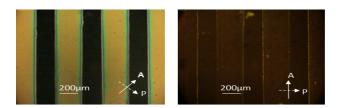


Figure 8. The images of the LC phase grating observed by a crossed polarizing optical microscope.

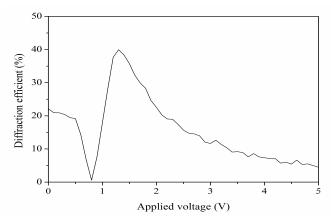


Figure 9. The first-order diffraction efficiency as a function of the applied voltage.

## 4. CONCLUSION

We have developed two approaches for controlling the pretilt angle of the LC alignment layers by using the conventional PI material. The proposed methods are compatible with current methods familiar in the LCD industry. The LC devices, such as LCFL and LC phase grating, are demonstrated in this work by using the proposed techniques. Other LC devices, for example no-bias OCB LCDs and bistable bend LCDs, can be fabricated by these novel techniques. A future study should examine the long-term stability of these modified PI films.

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