New Carbon Nanotubes UV Polarizer for Photoalignment of Liquid Crystals

*Hoon Sub Shin[1,2], Yuri Won[1], Ramesh Manda[1], Mira Jo[1], Tae Hyung Kim[1], Young Jin Lim[1] and Seung Hee Lee[1]**

[1]Applied Material institute for BIN Convergence, Department of BIN Convergence Technology and Department of Polymer Nano-Science and Technology, Jeonbuk National University, Jeonju, Jeonbuk 54896, Korea

[2]LG Display Co., Ltd., Gumi, Gyungbuk, 39402, Korea

*lsh1@jbnu.ac.kr

Abstract

We propose a unidirectionally aligned multi-layered carbon nanotubes (CNT) as a UV polarizer for LC photoalignment, which can replace wire-grid-polarizer (WGP) with high cost. A 12 multi-layered CNT polarizer exhibits the degree of polarization up to 91%. The fringe-field switching (FFS) LC device made by photoalignment with use of the proposed CNT polarizer exhibit uniform LC alignment in whole area and excellent electro-optics. The work proposes not only cost-effective novel polarizer replacing WGP for photoalignment of LC but also for photonic component of broadband polarizer from UV to IR.

Author Keywords

Carbon nanotube (CNT); Optical materials; Photoalignment; Polarizer.

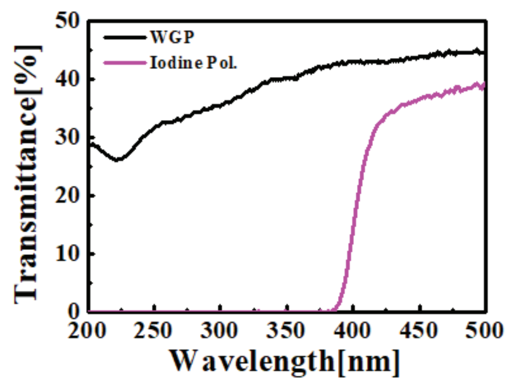

Figure 1. Wavelength-dependent transmittances of WGP and iodine polarizer

1. Introduction

Nowadays, LCDs are applied to all display applications such as TV, monitor laptop PC, smart phones, and automotive products because LCDs exhibit excellent electro-optic performances such as a high image quality and long-life time reliability. But recently, the adoption of OLED has been increased due to its high contrast ratio and flexibility in form factor. LCDs are continuously improving to overcome the relatively insufficient characteristics of OLEDs such as fast response time [1,2] and quality of alignment layer to improve the image quality [3,4]. The traditional rubbing polyimide approach is inefficient for these properties. Especially, the UV alignment technique are potential to high image quality because it does not cause light leakage due non-mechanical damage to the alignment layer and substrate, also no charge traps on the substrate [5]. Therefore, the image quality of the LCD can be greatly improved. The wider and symmetric viewing angles can also be achieved by decreasing the pretilt angle closed to zero degree. The asymmetry color shift of the viewing angle can be overcome by adopting novel electrode structures of IPS, FFS, and VA and enabling them into multi domain structures [3,4]. However, a linearly polarized UV light is required for photo-alignment. Because it just needs one direction to align, exposure of linearly polarized light makes selective photo excitations of the molecules of the alignment material possible [5]. For photoalignment, nanowire-grid polarizer (WGP) is generally used for this purpose [6] because iodine polarizers are impossible to polarize UV light less than 380nm due to strong UV adsorption of iodine molecules (see Figure 1). However, WGP requires to have a very short pitch of about 100 nm to make UV light linearly polarized, which is highly cost process due to nanopattern of metals [7].

In this regard, unidirectionally oriented CNT bundles are proposed which shows a strong optical activity and anisotropic behavior with visible and ultraviolet wavelengths. In addition, a film prepared by oriented CNT bundles shows a high transparency at shorter wavelengths of 380 nm and even less. Furthermore, oriented CNT film exhibits 75-80% of DOP in the region of 350nm ~ 800 nm and provides wide absorption spectrum due to the π -plasmon of graphite [8, 9]. Moreover, the DOP and optical activity of aligned SWCNT can be further enhanced by improving the degree of alignment of CNT by stretching the polyvinyl alcohol substrate [9].

In this paper, the multi-layered CNT sheet which acts as an efficient UV polarizer is demonstrated. The proposed multi-layer CNT polarizer is showing high DOP of ~91% in ultraviolet region and is used as photomask for photo-aligning of reactive mesogen (RM)-doped polyimide (RM-PI) (Nissan Chemical Co., Japan) [10] that provides efficient LC molecules alignment. The fabricated FFS device [11] with photo-alignment of RM-PI through 12-layered CNT polarizer exhibits comparable electro-optics to that made with WGP. The electro-optics of the device dependent on number of CNT layers in multi-layered CNT sheet is studied in detail.

2. Experimental

We prepare a multi-layer CNT polarizer by depositing number of CNT layers one over another on a Silicon substrate by chemical vapor deposition technique (A-tech system Co., Korea). And then a bundles of CNTs are unidirectionally stretched to make the CNT sheet by using a mechanical rotation tool. The long axis of CNT rods in each sheet is orient parallel to the stretching direction. Then the CNT sheets are stacked one over another and transferred to glass substrate as indicated in Figure 2(a). The obtained multi-layer CNT polarizer is also utilized for manipulating the orientation of nematic LC through photo-alignment of RM-PI mixture (Nissan, Japan)[10]. The complete experimental procedure for making multi-layered CNT film and a photo-alignment of RM-PI is schematically illustrated in the Figure 2. We have employed FFS cell which consist of both patterned pixel and non-patterend common electrodes on bottom substrate while no electrodes on the top substrate [11]. The substrate dimensions follows: length:width:thickness = 3 cm:3 cm:2 mm. The pixel and common electrodes are separated by very thin passivation layer with thickness of approximately 0.5 µm. The pixel electrode stripes are separated by the 4.5 µm with uniform width of 3.5 µm. The separation between the two glass substrates is fixed to 3.4 µm with film spacers.

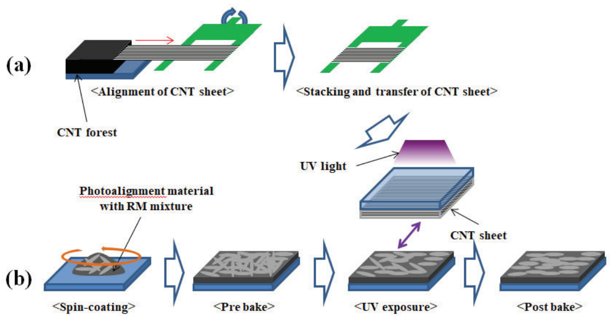

Figure 2. The schematic of experimental procedure for making anisotropic molecular arrangement in a photoalignment layer with CNT sheet: (a) CNT sheet is drawn from the grown CNT forest and then transferred to a glass substrate and (b) Detailed process how to get photo-alignment layer with anisotropy.

A nematic LC with positive dielectric anisotropy of 4.7 and birefringence of 0.115 (JNC Corp., Korea) is employed in this report. Firstly, the RM-PI mixture is spin coated on both substrates of FFS cell and followed by the pre-bake for 90 s at 80°C to evaporate the solvent. The temperature of the sample is accurately maintained by temperature controller. Next, we perform UV irradiation to RM+PI layer by controlling the polarization direction of the incident UV light with our multi-layer CNT film. The CNT film with 3/5/8/12 layers was used for controlling the polarization state of the incident light. The CNT sheet is fixed top of the cell at which portion of the UV light with known polarization direction passes thorough CNT and then incident on the cell while another portion of the light is absorbed or reflected back. The incident angle of UV light is normal to the cell's substrate. We have used 365nm UV light (Hamamatsu Photonics K.K, Japan) with intensity of 75 mJ (5 mW/cm2) for 15 s at room temperature. Further, the post-bake was performed at 130°C for 10 min to remove impurities and rearrange the reactive monomer molecules. Finally, two substrates are assembled one over another and the liquid crystal infiltration was performed by capillary action at isotropic temperature of the nematic LC.

3. Results and discussion

Figure 3(a) shows the optical microscope images of prepared CNT polarizer as a function of number of CNT layers. Here, the polarization direction of incident UV light is set to perpendicular to the CNT orientation. The transmittance of the prepared polarizer is compared with the traditional iodine-based polarizer (LG Chem., Korea). One can easily notice that the relative transmittance of CNT polarizer within visible region decreases with increasing number of CNT layers. Further, number of dark lines along the CNT's stretching direction, which comes from a adsorption of incident linearly polarized light, is increasing with number of CNT layers. Most of the area cover by the dark lines for 12-layer CNT. As one can easily notice from the wavelength-dependent transmittance of this film depicted in Figure 3(b), the transmittance of CNT polarizer at 365 nm is measured to be >10%, 6.5%, 1.0% and 0.5% for 3, 5, 8, and 12 CNT layers, respectively. The iodine polarizer is exhibiting almost zero transmittance. However, the proposed CNT polarizer is capable to extend the attenuation of incident light up to deep ultraviolet region providing a wider operating wavelength range from 300 nm to 400 nm. Further, we measure a degree of polarization (DOP) which indicates its polarizing capability, defined as,

$$DOP = \sqrt{\frac{T_{\parallel} - T_{\perp}}{T_{\parallel} + T\perp}} \times 100 \qquad (1)$$

where $T_{\parallel}$ and $T_{\perp}$ are transmittances of the CNT polarizer when it is aligned parallel and perpendicular to the plane of polarization of incident light, respectively. Interestingly, the DOP is increased from 54.1% to 91.3%, at 365 nm, by increasing the number of CNT sheets from 3 to 12, as shown Figure 2(c). This results implies that the CNT polarizer with densely packed CNT layers in series with matching orientations is effectively performing attenuation of incident polarized light in the direction perpendicular to the CNT stretching, therefore, resulted to a good polarized light at 365 nm.

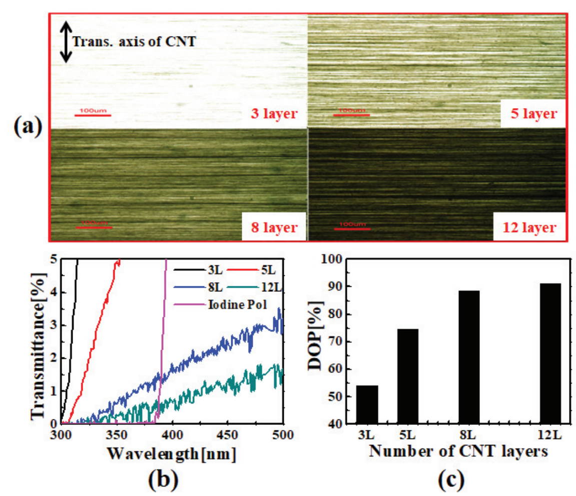

Figure 3. (a) Optical microscope images of prepared multi-layered CNT sheets. (b) Wavelength-dependent transmittances of each CNT sheet and Iodine Polarizer. (c) Calculated DOP of CNT sheet as a function of number of CNT layers at 365nm.

In order to investigate how DOP of the CNT polarizers affect alignment of mesogen in the photo-alignment of RM-PI, the POM characterizations were performed. In a first case, the nonpolarized UV irradiation was performed directly to the substrate. In second case, the irradiation of UV was performed through our multi-layer CNT polarizer positioned above the substrate. The POM images in Figure 4(a) and 4(b) indicates that no preferred orientation of polymerized mesogen is achieved. However, POM images in Figure 4(c) and 4(d) clearly exhibits extinction and bright state when the polarizing direction of CNT polarizer is coincident and makes 45° with crossed polarizers, respectively, indicating an orientational ordering of polymerized mesogen in unidirection is achieved. Conclusively speaking, the photoalignment layer becomes optically anisotropic after UV exposure through multi-layered CNT sheet, that is, the CNT sheet produces the linear polarized state in a UV region enough to induce anisotropic orientation of mesogen.

We further have measured retardation of the photoaligned RM-PI layer in a wavelength range from 450 nm to 720 nm. The obtained retardation is 11 nm, 21nm, 42, nm, 46 nm, 55nm for CNT polarizer with 3, 5, 8, 12 layers and WGP at 550nm, respectively, as shown in Figure 4(e) and 4(f). Clearly, the retardation increases with increasing number of CNT layer, which makes sense because the DOP follows the same trend. Higher retardation attributed from highly oriented CNT which is expected to give a better homogenous LC alignment. The retardation achieved by conventional WGP is 55 nm at 550nm, which is slightly larger than that with 12 CNT layers.

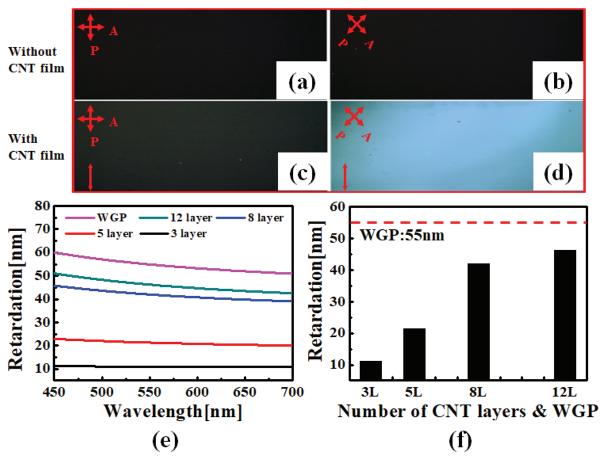

Figure 4. POM images of RM+PI layers polymerized without CNT film [(a) and (b)], and with CNT film [(c) and (d)]. Under exposure of nonpolarized UV, no birefringence in photoalignment layer is induced ((a) and (b)) while the birefringence coming from orientational ordering of mesogen in the layer is clearly induced ((c) and (d)).P and A represents the polarizer and analyzer of POM and the arrow indicates a polarizing direction of CNT polarizer with 5 layers. Measured wavelength-dependent retardation (e) and retardation at 550 nm (f) of photoalignment layer with conventional WGP (Edmund Optics, USA) and CNT sheets consisted of 3, 5, 8, and 12 layers.

Motivated by these results, we have prepared FFS-LC cells and investigated their electro-optics while applying a square-wave with 1 kHz, in which initial LC orientation is set to 7° with respect to the signal electrode direction. Very interestingly, all FFS cells show a good dark state irrespective of number of CNT layers in the CNT polarizer, as shown in POM images of Figure 5 (a)-(d). Nevertheless, POM images in field-on state show distinct behavior between cells. For instance, the FFS cells exposed with 3 and 5 CNT layer are exhibiting slight nonuniformity in brightness called mura at 3 V, whereas the cells exposed with 8 and 12 CNT layers do not show such mura (see magnified right image in Figure 5(e)).

We infer that the mura at 3V is associated with low DOP of the CNT polarizer because the lower the DOP the orientation of the CNT deviates more from mean orientation or the absorption of UV along the CNT stretching direction is lower, as proven by nonuniform dark lines in Figure 3(a). In other words, the orientation ordering of RM induced by CNT sheet is not uniform enough from position to position, giving rise to nonuniform azimuthal anchoring strength. Therefore, we expect the UV exposure with low DOP CNT polarizer can induce uniform LC optic axis but its anchoring strength is not uniform enough dividing regions into weak and strong anchoring, which correlates with nonuniform dark lines; however, the DOP more than 85 % for 8 and 12 layered CNT polarizers is good enough to induce both uniform optic axis and anchoring strength of LC.

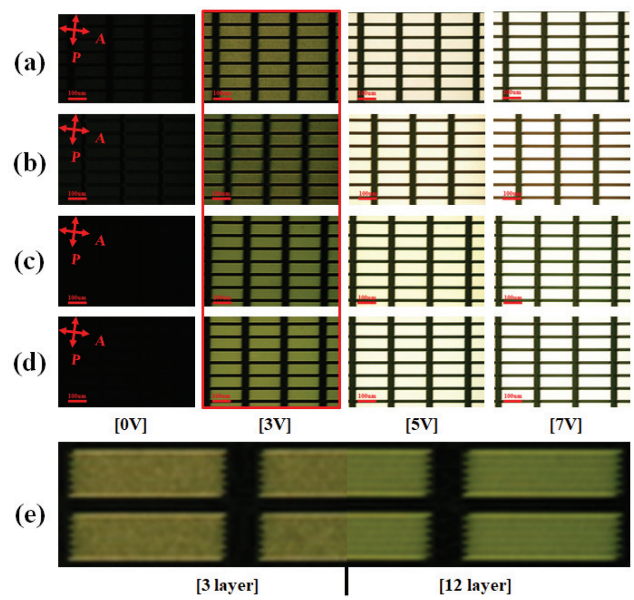

Figure 5. POM images while increasing voltages from dark to white states in UV-aligned FFS cells by CNT sheets with different CNT layers: (a) 3layer, (b) 8layer, and magnified one pixel images at 3 V of 3 layer and 8 layer.

At the final step, the response time of the FFS cell is measured as a function of CNT layers. The rising time (τ_{on}) and falling time (τ_{off}) are defined as the time required for changing the transmittance from 10% to 90% and 90% to 10%, respectively. The falling time is mainly associated with elastic relaxation of LC molecules back to original position upon voltage withdrawn. The τ_{on} and τ_{off} times are derived from dielectric response and director relaxation dynamics, which is expressed as [12],

$$\tau_{on} = \frac{\gamma_1}{\varepsilon_o|\Delta\varepsilon|E^2 - \frac{\pi^2}{d^2}K_{22}} = \frac{\gamma_1}{\varepsilon_o|\Delta\varepsilon|E^2 - 2\frac{W}{d}}, \quad (2)$$

$$\tau_{off} = \frac{\gamma_1 d^2}{K_{22}\pi^2} = \frac{\gamma_1 d}{2W} \quad (3)$$

where, $\gamma 1$ is a rotational viscosity, K22 is a twist elastic constant, E is an electric field strength, d is a cell gap, $\Delta\varepsilon$ is a dielectric anisotropy of LC, and W is a surface anchoring energy of LC molecules with alignment layer. As understood from the Equation (2) and (3), the alteration in both τ_{on} and τ_{off} originate from difference in anchoring strength of LC to the photoalignment layer since the same LC is used in all cells.

The τ_{on} and τ_{off} of WGP sample are measured to be 7.5 ms and 12.8 ms, respectively. Interestingly, τ_{off} of the FFS cell decreases with increasing CNT layers such that it is 28.8 ms for 3 layers but 13.1ms for 12 layers of CNT, whereas the τ_{on} is mostly unaltered, as shown in the Table 1. As can be understood from the Equation 3, stronger the anchoring energy, the τ_{off} becomes shorter so that we can conclude that the anchoring energy with 12 CNT layers is comparable to that in WGP, indicating the CNT polarizer with 12 layers can replace high cost WGP.

Finally, we are working on improving the DOP of CNT polarizer by controlling density of grown CNT forests by chemical vapor deposition and stretching method because higher DOP gives rise to higher induced retardation in the applied photoalignment layer, which results in better LC alignment and fast falling time.

Table 1. The rising (τ_{on}) and falling (τ_{off}) response time of the FFS cell for different CNT layers and WGP

Samples	Rising Time(τ_{on})	Falling Time(τ_{off})
3 layer	5.8ms	28.8ms
5 layer	6.5ms	21.7ms
8 layer	6.9ms	16.1ms
12 layer	6.9ms	13.1ms
WGP	7.5ms	12.8ms

4. Impact

We propose a multi-layer CNT based UV polarizer which exhibits higher DOP of 91% by matching orientation of stacked CNTs in each layer. A novel approach for LC alignment is demonstrated through photoalignment of RM-PI by utilizing multi-layer CNT polarizer that can be utilized for FFS-LCD. Although, the RM-PI layer photoaligned through 3-layered CNT polarizer exhibits a low gray mura and relatively slow response time, a CNT polarizer with more layers, for instance, 8 and 12-layered CNT polarizers, exhibit excellent uniformity in LC alignment and good electro-optics. For the first time to our knowledge, we propose the multi-layer CNT polarizer applying for photoalignment layer of LC, which can replace the conventional high cost WGPs and we believe it has strong potentiality to utilize in future photonic and electro-optic devices with broad band gap from UV to infrared.

5. Acknowledgements

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