Ultrafast laser induced nanostructured ITO for liquid crystal alignment and higher transparency electrodes

Solodar, A.; Cerkauskaite, A.; Drevinskas, R.; Kazansky, P. G.; Abdulhalim, Ibrahim

2018

Solodar, A., Cerkauskaite, A., Drevinskas, R., Kazansky, P. G., & Abdulhalim, I. (2018). Ultrafast laser induced nanostructured ITO for liquid crystal alignment and higher transparency electrodes. *Applied Physics Letters*, 113(8), 081603-. doi:10.1063/1.5040692

<https://hdl.handle.net/10356/88512>

<https://doi.org/10.1063/1.5040692>

© 2018 The Author(s). All rights reserved. This paper was published by AIP Publishing in *Applied Physics Letters* and is made available with permission of The Author(s).

Downloaded on 26 Apr 2023 20:21:28 SGT

Ultrafast laser induced nanostructured ITO for liquid crystal alignment and higher transparency electrodes

A. Solodar,¹ A. Cerkauskaitė,² R. Drevinskas,² P. G. Kazansky,² and I. Abdulhalim^{1,3,a)}

¹Department of Electro-Optics and Photonics Engineering and The Ilse Katz Institute for Nanoscale Science and Technology, Ben Gurion University of the Negev, Beer Sheva 84105, Israel

²Optoelectronics Research Centre, University of Southampton, Southampton SO17 1BJ, United Kingdom

³SHARE-NEW CREATE Programme, School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798

(Received 19 May 2018; accepted 12 August 2018; published online 23 August 2018)

Femtosecond laser nanostructured indium tin oxide (ITO) coated glass is shown to act both as a liquid crystal (LC) alignment layer and as an electrode with higher transparency. The nanopatterns of the 120 nm period were created using ultrashort laser pulses directly on ITO films without any additional spin coating materials or lithography process. Nine regions of laser-induced nanostructures were fabricated with different alignment orientations and various pulse energy levels on top of the ITO confirming the follow-up of the LC director to the line orientation. The device interfacial anchoring energy was found to be $\sim 1 \mu\text{J}/\text{m}^2$, comparable to the anchoring energy of nematic LC on photosensitive polymers. The transparency as an electrode was found to improve due to the better antireflection and lower absorption expected from a nanostructured surface. *Published by AIP Publishing.*

<https://doi.org/10.1063/1.5040692>

Photonic devices based on liquid crystals (LCs) are continuously rising due to their strong electro-optic effects and their mature technological status in display systems starting from phase modulators, tunable filters, polarization rotators, tunable lenses, and other light manipulation devices for the optical telecommunication industry.¹ Particularly, LC spatial light modulators (SLMs) and tunable lenses are expected to be part of each augmented reality goggles and digital camera in the near future.^{2,3} However, there is a continuous need to improve the quality of these devices, particular contrast, speed, and the ability to form aligned LC layers on curved surfaces. In LC displays (LCDs), there is still a place to improve the energy consumption when compared to their counterparts, the light emitting diode displays. The routes to improve LCDs for both display and photonic devices are by the improvement of the LC materials, invention of novel electro-optic effects and photonic designs, improvement of the alignment layer, and the use of higher transparency electrodes. In this work, we report on the creation of nanograting (~ 120 nm pitch) in indium tin oxide (ITO) layers using ultrashort pulses of a femtosecond laser and its use as an alignment layer for liquid crystals exhibiting also higher transparency. Hence, this methodology should have potential for improved LC devices, for creation of novel devices, for example, by nanostructuring on curved surfaces, and for better energy consumption displays. As a more transparent ITO electrode, other applications are possible in energy devices such as photovoltaic and photocatalytic devices. The physics behind LC alignment is of high interest as well because it teaches about the interaction of molecules with surfaces and reveals the hydro-philic/phobic surface properties.

The most popular alignment technique in LC industry comprises unidirectional mechanical rubbing of thin polyimide or polymer coating.⁴ These thin films are spin coated

and then cured at appropriate temperature according to the polyimide type. Thereafter, the cured films are rubbed with a velvet cloth, producing micro- or nano-grooves along the rubbing direction to which the LC molecules are then aligned. However, the rubbing method has some shortcomings, due to electrostatic charge accumulation, surface damage, and particle dust generation, as a result of the mechanical contact interaction between the cloth and the surface during the rubbing process.⁵ Liquid crystal molecules can also be aligned by noncontact methods, such as photoalignment by illumination with ultraviolet polarized light of photosensitive polymers, chemically by surface active agents (surfactants), or by ion beam irradiation.⁶ However, these techniques are not widely implemented in the industry, because of insufficient time stability, lower anchoring energy, and requirement of expensive vacuum equipment.^{7,8}

In recent years, new alignment methods were investigated, utilizing nanomaterial structures based on Berreman's groove theory.⁹ Homogeneous, tilted, and homeotropic alignment of nematic LC molecules using nanometer-sized ultrafine grooves fabricated on ITO substrates was demonstrated using electron beam lithography.¹⁰ In addition, nanoscale patterns can also be employed for LC alignment by nonlinear laser lithography (NLL) on a titanium (Ti) coated glass substrate¹¹ or by the nanoimprint lithography method.¹² Additional nanostructured alignment method was presented utilizing tilted ITO line patterns in order to reduce the switching time effects.¹³ Despite the great potential of the methods mentioned above, their fabrication process is still quite complicated and requires several steps in the fabrication process such as photoresist spin coating, lithography process, mould structure design, and heating.

Recently, we have shown that it is possible to obtain nanostructuring of the ITO surface with direct fs laser writing exhibiting relatively high form birefringence that was demonstrated useful for permanent storage of data.¹⁴ In addition, the nanopatterned ITO film exhibited improved transparency.

^{a)}Author to whom correspondence should be addressed: abdulhlm@bgu.ac.il

In this letter, we demonstrate LC alignment on top of such nanostructured ITO with the advantage that it also acts as the electrode layer with higher transparency as compared to the closed ITO film.

Two LC devices were built, each comprises $17 \times 15 \times 2.5 \text{ mm}^3$ ITO coated glass substrates on either side of the device, with $145 \pm 10 \text{ nm}$ thickness. The substrates were initially cleaned by an ultrasonic bath with the three step process: deionized (DI) water, isopropanol (IPA), and at last with acetone, where each stage lasts about 20 min at a temperature of 50° . Then, cotton wipers with cleaning solvents were used in order to remove any unwanted materials on the surface of the glasses. The ITO patterning of each of the devices is different as well as the LC orientation and therefore will be described separately. The aim of the 1st device was to demonstrate the different alignment configurations, while the aim of the 2nd device was to show that large area devices can be built using this methodology.

The first device under test (FDUT) consists of nine squared nanostructured regions at different grating orientations on one glass substrate from one side and a uniform ITO coated glass substrate from the other. The square zones are separated by a uniform ITO region, where the dimension of each square is $2 \text{ mm} \times 2 \text{ mm}$. The nanostructured regions were created by femtosecond laser system PHAROS (Light Conversion Ltd.) operating at a wavelength of 1030 nm with the repetition rate of 200 kHz and the pulse duration of 300 fs . The squares were printed by scanning the sample at the speed of 1 mm/s with the interline distance of $2 \mu\text{m}$. Each row of the square nanostructure matrix was fabricated under different pulse energies of 67.5 nJ , 60 nJ , and 52.5 nJ focused by a 0.16 numerical aperture (NA) objective as depicted in Fig. 1. Different pulse energies influence the depth of the nanogrid patterns, causing various retardation levels in the specific regions. The orientation of the nanograting at each column was changed from horizontal to diagonal and to vertical by rotating a half waveplate, to achieve different alignment directions as illustrated in Fig. 1. The generated ITO nanograting patterns on the glass surface are illustrated in the images taken using an atomic force microscope (AFM) in Fig. 2. The theory behind the origin of fs laser induced nanogratings is not well understood yet and outside the scope of this paper, and the readers are referred to this review on this intriguing phenomenon.¹⁵

FIG. 1. Femtosecond laser nanostructuring of nine ITO regions imprinted under different writing conditions. The red lines represent the nanostructure orientation, while the blue arrows represent the polarization direction of the laser beam. The colors represent different retardation levels in nm (thickness times the form birefringence), which was imaged by the quantitative birefringence measurement system. The scale bar is 0.5 mm .

FIG. 2. AFM images of the uniform ITO film (a) and the generated nano-grooves by the fs laser (b). The laser pulse energy was $0.76 \mu\text{J}$. The scale bar for (a) is $0.5 \mu\text{m}$.

The uniform ITO substrate was additionally cleaned using an ultra violet ozone cleaning system (UVOCS) for 50 min in order to achieve a high hydrophilic surface with a small contact angle during the spin coating of the polymer alignment layer. Then, a sensitive polymer layer ROP-108 (approximately 30 nm thick), obtained from Rolic-Switzerland, was spin coated on the ITO uniform film glass substrate.

After coating, the uniform ITO substrate was baked 15 min at 180°C and then slowly cooled down to room temperature. Thereafter, linearly polarized ultra-violet (UV) light of power density of 0.5 mW/cm^2 for 20 min was used. Then, the two substrates were sandwiched together with $10\text{-}\mu\text{m}$ spacers. During the construction, a special emphasis was considered on the thickness variation across the cell in order to reduce to minimum any wedge formations that can cause non-uniform retardation and response time. After assembly, the gap was filled by capillary suction with E-7 LC (Merck). Finally, two electrodes were connected to the substrates. Following this process, nine different squared alignment regions of homogeneously aligned (parallel or anti-parallel geometry), 45° and 90° twisted nematic devices were achieved. It is important to emphasize that the nanogrid patterns during this work generated strictly on the ITO films by the fs laser without any additional lithographic process, spin coating materials, or rubbing treatments. The fact that these different alignment regions are obtained with good quality alignment (see Fig. 3) indicates that the LC director on the patterned surfaces follows the direction of the nanogrooves of the gratings as expected from Berreman's theory.

For the FDUT inspection, a polarizing microscope was used in order to examine the different alignment regions. It is noteworthy that the molecules align themselves with the direction of the nanogrid tunnels from the one side and along

FIG. 3. (a) Transmission results of the nine different regions observed under a polarized microscope. Each column represents different LC alignment modes written at different pulse energies by the fs laser along each row as illustrated in Fig. 1. The red bar represents 0.1 mm , and green bars represent the alignment direction of the nanogrid patterns. (b) Schematic of the constructed device. The inset shows polarized microscopy images of a central region at different voltages for the 45° twisted mode. The black scale bar represents 0.5 mm .

the polymer alignment axis from the other side of the device. In the case of parallel/anti-parallel alignment, under crossed polarizers, the light transmitted through the device did not change its polarization direction, so that the light which reaches the analyzer cannot pass through it. In the case of a twisted 45° alignment device, the incoming linear polarized light coincides with the polymer substrate alignment direction. Therefore, the linear polarized light entering through the polymer coated substrate will follow the twist and be rotated 45° by the time it reaches the nanogrid patterned substrate. Upon transmission, the polarization direction will be rotated by 45° so that the outgoing light will partially pass through the analyzer. According to the same principle, an incoming linearly polarized light transmitted through the twisted 90° alignment region will follow the twist of the LC director. This leads to a rotation of the output polarization state along the analyzer (rotation of 90°), which ensures a total transmission of the outgoing light through the analyzer.

Figure 3(a) shows a variety of output extinction states obtained by the microscope camera under crossed polarizers, while Fig. 3(b) demonstrates the reflection intensity from the central region for various applied voltages. This proves that the LC molecular director follows the direction of the nanogrooves as it is expected from Berreman's groove theory.⁹

The measured transmission spectra of the nine regions between crossed polarizers and an angle of 45° between the polymer alignment axis and the polarizer at various applied voltages are shown in Fig. 4, while Fig. 5 demonstrates a voltage-dependent amplitude modulation for three different wavelengths.

As can be seen from Figs. 4 and 5, in the region that was written with 67.5 nJ (PA-67.5 nJ), the molecules start orienting at relatively low threshold voltage (0.5 ± 0.1 V), which is smaller than the expected threshold voltage (~ 1 V) for LC E-7. The PA-60 nJ region exhibits a higher threshold voltage (~ 0.9 V), while the PA-52.5 nJ region did not respond to the applied voltage for all alignment regions. Lower threshold voltage indicates weaker anchoring energy, which is characterized, *inter alia*, by higher relaxation time.

For measuring the relaxation time, a collimated laser diode with a wavelength of 633 nm was used as a light source, while the LC device was placed under crossed

FIG. 4. FDUT spectrometer readout. Transmission spectra for various alignment regions at different applied voltages (sine wave at 1 kHz) between crossed polarizers. The green bars represent the orientation of nanograting patterns.

FIG. 5. FDUT voltage-dependent transmission readout. Transmission spectra for various alignment regions as a function of voltage (sine wave at 1 kHz) for three different wavelengths (485 nm, 525 nm, and 625 nm) between crossed polarizers. The green bars represent the orientation of nanograting patterns.

polarizers oriented at 45° with respect to the polarizer axis. A sinusoidal 1 kHz with 1 V_{amp} wave modulated by a low frequency square wave, generated from an arbitrary wave form generator, was applied to the device. The transmitted intensity was monitored with a photodetector connected to an oscilloscope. Based on the experimental results, the measured relaxation time is 330 ms and the rise time is 80 ms. Despite the relatively high response times, these are still in the plausible range for thick LC devices.

In order to evaluate the anchoring energy (W_a) between the nematic LC molecules and the nanogrid substrate, we used the improved high electric field method.¹⁶ The measured polar anchoring energy from the PA-60 nJ alignment region was on the order of 1.063×10^{-6} J/m². This anchoring energy is comparable to that measured using photo-aligning polymer materials, which is usually in the range of 10^{-5} – 10^{-6} J m⁻².^{7,8} As it is well known from Berreman's theory, the azimuthal anchoring energy on a nanostructured periodic surface can be determined from¹⁷

$$W_a = \frac{2\pi^3 K A^2}{\Lambda^3} \left(1 + \frac{\pi K}{\Lambda W_p} \right)^{-1}. \quad (1)$$

Here, Λ and A are the grating period and depth, respectively, W_p is the polar anchoring energy, and K is the average elastic constant of the splay and bend. In our case, $\Lambda = 120$ nm, $A \sim 50$ nm, and for LC E-7 with elastic constants: $k_{11} = 10.8$ pN and $k_{33} = 17.5$ pN, and we obtain the azimuthal anchoring energy W_a to be around 3.63×10^{-6} J/m².

Another important parameter describing the device quality is the contrast ratio. To evaluate the contrast ratio, the device was placed between crossed polarizers at 45° with respect to the polarizer axis. The transmission versus voltage was measured by the photodetector, while the He-Ne laser was used as a light source. The measured contrast ratio was around 30:1 for the TW45-60 nJ alignment region. As it is seen from the top and middle rows of Fig. 3(a), the contrast ratio is moderate, possibly influenced by the nanoscale inhomogeneity of the nanograting surface. On the other hand, the PA-52.5 nJ region (bottom row) from Fig. 3(a) exhibits a good dark state, which indicates that the contrast ratio can be increased during the further optimization process. This was achieved also in the next device even over a larger area.

The second device under test (SDUT) was constructed completely from two ITO nanograting patterned glass substrates. In order to achieve faster laser material processing, the ITO substrates were irradiated by a femtosecond laser system operating at a wavelength of 1030 nm with the repetition rate of 500 kHz and the pulses with a duration of 400 fs focused via 0.03 NA focusing lens. The nanograting patterns on the two ITO substrates were fabricated under pulse energies of $0.76 \mu\text{J}$ and $0.68 \mu\text{J}$, respectively, over $12 \times 12 \text{ mm}$ area, by scanning the samples at the speed of 1 mm/s [Fig. 6(a)]. Then, the two substrates sandwiched together with parallel/anti-parallel orientation alignment, separated by $10 \mu\text{m}$ spacers. Finally, LC BL036 was inserted into the cell in the isotropic phase by capillary action. Figure 6(b) describes SEM images at the border between the uniform ITO and nanograting regions, while Figs. 6(c) and 6(d) illustrate the border region of the SDUT rotated by 45° under a polarized microscope. Without voltage bias [Fig. 6(c)], the aligned liquid crystal molecules in the nanogrid region exhibit maximum transmission intensity, while in the uniform ITO region, the light was blocked by the polarizers.

Upon voltage activation [Fig. 6(d)], the aligned LC molecules in the nanogrid region were stimulated by the applied electrical field. As a result, the reflected spectrum colour in the nanogrid region gets changed, depending on the voltage, while the ITO uniform region remains colorless. Furthermore, this large area device was examined at various supplied voltages with the same microscope as used in the experiment of Fig. 3, but in the reflection mode as illustrated in Fig. 7. The reflectivity results reveal a uniform extinction, when the LC device optical axis is parallel to the axis of one of the polarizers (0°). Furthermore, when the device is placed with its optical axis 45° from the polarizer's axis, it exhibits a uniform reflection change as a function of voltage. Note the excellent extinction at zero voltage on the top right image.

FIG. 6. ITO grid substrate (a) and SEM images of the nanostructured region (b). The red dashed line represents the border between the uniform ITO surface (left) and nanograting patterns (right). Alignment behavior of the second device (rotated by 45°) with two nanogrid substrates under crossed polarizers without voltage (c) and under bias of 8 V, 100 Hz, and 1 V offset (d).

FIG. 7. Illustration of reflection from SDUT under a polarized microscope with crossed polarizers. (a) Linear polarized light (P) reflected from the device, oriented at 45° with respect to the polarizer axis. The reflected light reaches the analyzer (A) through the beam splitter (only for illustration purpose) toward the camera. (b) The device was examined under various applied voltages.

In addition, the transmission spectrum through the SDUT, placed at 45° between crossed polarizers, was measured for normal incidence at different voltages as illustrated in Fig. 8(a). Furthermore, Fig. 8(b) demonstrates the transmission as a function of voltage for three different wavelengths, while Fig. 8(c) illustrates the retardation deduced from Fig. 8(a) for three different wavelengths.

The nanograting patterns consist of alternating regions of 145 nm ITO lines and glass substrate (or a few nanometer thickness residual ITO). Thus, the transmittance of incident light is expected to be higher than those of a uniform ITO layer in typical liquid crystal devices. As a proof of principle, the transparency in the center grid region and at the outside area was measured, as depicted in Fig. 8(d). The results show around 3% higher transmittance at the TW45 60 nJ of the FDUT grating region starting above the wavelength of 650 nm and about 10% higher transmittance through the LC device with two ITO nanogrid substrates (SDUT) written under fs laser pulse energies of $0.76 \mu\text{J}$ and $0.68 \mu\text{J}$, respectively. The higher transparency can be understood easily from the fact that the nanostructured surface has lower effective refractive indices for both polarizations TM and TE

FIG. 8. SDUT spectrometer readout. Transmission spectra of SDUT at different applied voltages (a). Transmission spectra as a function of voltage (b) and retardation as a function of voltage (c) for three different wavelengths. Transparency measurement without polarizers of the central region of FDUT (TW 45 60 nJ) and SDUT, compared to uniform ITO region (d).

(parallel and perpendicular to the lines), and therefore, Fresnel reflections are lower.¹⁸

In addition, a lower amount of material due to the spaces between the ITO lines causes less absorption. This fact is highly important for integrated optical devices and devices in the infrared range when the absorption of the ITO film becomes the main cause of reduced transparency, for example, when developing liquid crystal tunable filters based on guided mode resonance or improving the lateral resolution of optically addressed spatial light modulators.^{19,20}

In conclusion, nanopatterned ITO was achieved using a femtosecond pulsed laser exhibiting higher transparency and acting as an alignment layer for liquid crystals. This type of substrate could have great potential for lowering the energy consumption of LCD technology, for preparing LC photonic devices with lower losses such as guided wave LC devices and resonance based devices, and for forming alignment layers on curved surfaces with almost any required shape. Another important use is in the emerging field of tunable metamaterials by modifying surfaces coated with ITO in a variety of ways as ITO becomes plasmonic in the near infrared with a near zero refractive index at a certain wavelength.^{21–23}

This research was supported partially by the National Research Foundation, Prime Minister's Office, Singapore, under its Campus for Research Excellence and Technological Enterprise (CREATE) program and Engineering and Physical Sciences Research Council (EPSRC) (EP/M029042/1). The data for this work are accessible through the University of Southampton Institutional Research Repository. doi: 10.5258/SOTON/D0199. We are thankful to Rolic-Switzerland for providing the photoalignment layers.

- ¹L. Vicari, *Optical Applications of Liquid Crystals* (Institute of Physics Publication, Bristol, Philadelphia, 2003).
- ²R. E. Stevens, T. N. L. Jacoby, I. S. Aricescu, and D. P. Rhodes, *Proc. SPIE* **10335**, 103350Q (2017).
- ³J. S. Chen and D. P. Chu, *Appl. Opt.* **55**(3), A127 (2016).
- ⁴J. Stohr, M. G. Samant, A. Cossy-Favre, J. Diaz, Y. Momoi, S. Odahara, and T. Nagata, *Macromolecules* **31**(6), 1942 (1998).
- ⁵I. Abdulhalim, *J. Nanophotonics* **6**, 061001 (2012).
- ⁶K. Takato, *Alignment Technologies and Applications of Liquid Crystal Devices* (Taylor & Francis, London, New York, 2005).
- ⁷O. Yaroshchuk and Y. Reznikov, *J. Mater. Chem.* **22**(2), 286 (2012).
- ⁸V. G. Chigrinov, V. M. Kozenkov, and H.-S. Kwok, *Photoalignment of Liquid Crystalline Materials: Physics and Applications* (Wiley, Chichester, England, Hoboken, NJ, 2008).
- ⁹D. W. Berreman, *Phys. Rev. Lett.* **28**(26), 1683 (1972).
- ¹⁰T. Kagaiyo, K. Fujibayashi, T. Shimamura, H. Okada, and H. Onnagawa, *Jpn. J. Appl. Phys., Part 1* **44**(1b), 578 (2005).
- ¹¹I. Pavlov, A. Rybak, A. Dobrovolskiy, V. Kadan, I. Blonskiy, F. Ö. Ilday, Z. Kazantseva, and I. Gvozдовskyy, *Liq. Cryst.* **45**(9), 1265 (2018).
- ¹²Y. J. Liu, W. W. Loh, E. S. P. Leong, T. S. Kustandi, X. W. Sun, and J. H. Teng, *Nanotechnology* **23**(46), 465302 (2012).
- ¹³W. B. Jung, H. S. Jeong, H. J. Jeon, Y. H. Kim, J. Y. Hwang, J. H. Kim, and H. T. Jung, *Adv. Mater.* **27**(42), 6760 (2015).
- ¹⁴A. Cerkaskaite, R. Drevinskas, A. Solodar, I. Abdulhalim, and P. G. Kazansky, *ACS Photonics* **4**(11), 2944 (2017).
- ¹⁵Y. Shimotsuma, P. G. Kazansky, J. R. Qiu, and K. Hirao, *Phys. Rev. Lett.* **91**(24), 247405 (2003).
- ¹⁶Y. A. Nastishin, R. D. Polak, S. V. Shiyankovskii, V. H. Bodnar, and O. D. Lavrentovich, *J. Appl. Phys.* **86**(8), 4199 (1999).
- ¹⁷S. Faetti, *Phys. Rev. A* **36**(1), 408 (1987).
- ¹⁸I. Abdulhalim, *Appl. Opt.* **46**(12), 2219 (2007).
- ¹⁹I. Abdulhalim, *Chin. Opt. Lett.* **7**(8), 667 (2009).
- ²⁰A. Solodar, T. A. Kumar, G. Sarusi, and I. Abdulhalim, *Appl. Phys. Lett.* **108**(2), 021103 (2016).
- ²¹A. Minovich, D. N. Neshev, D. A. Powell, I. V. Shadrivov, and Y. S. Kivshar, *Appl. Phys. Lett.* **96**(19), 193103 (2010).
- ²²X. Wang, D. H. Kwon, D. H. Werner, I. C. Khoo, A. V. Kildishev, and V. M. Shalaeв, *Appl. Phys. Lett.* **91**(14), 143122 (2007).
- ²³F. Zhang, Q. Zhao, L. Kang, D. P. Gaillot, X. P. Zhao, J. Zhou, and D. Lippens, *Appl. Phys. Lett.* **92**(19), 193104 (2008).