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View online: http://dx.doi.org/10.1063/1.4871255
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Liquid crystal terahertz phase shifters with functional indium-tin-oxide nanostructures for biasing and alignment

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(Received 17 February 2014; accepted 1 April 2014; published online 10 April 2014)

Indium Tin Oxide (ITO) nanowhiskers (NWhs) obliquely evaporated by electron-beam glancing-angle deposition can serve simultaneously as transparent electrodes and alignment layer for liquid crystal (LC) devices in the terahertz (THz) frequency range. To demonstrate, we constructed a THz LC phase shifter with ITO NWhs. Phase shift exceeding π/2 at 1.0 THz was achieved in a ~517 μm-thick cell. The phase shifter exhibits high transmittance (~78%). The driving voltage required for quarter-wave operation is as low as 5.66 V (rms), compatible with complementary metal-oxide-semiconductor (CMOS) and thin-film transistor (TFT) technologies. © 2014 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4871255]

In the past decade, several quasi-optic components using liquid crystals (LCs) for the terahertz (THz) wave, e.g., phase shifters,1–7 phase gratings,8 modulators,9 and polarizers,10,11 have been demonstrated. These devices are, in general, based on magnetically and electrically controlled birefringence of LCs.1–7 In our earlier work on electrically tunable phase shifters, a high driving voltage (~125 V (rms)) on the side electrodes was needed due to the lack of suitable materials as transparent electrodes in the THz frequency range.3,4 On the other hand, magnetically tunable devices function well, but these are not ideal for some applications because of the bulky design.2 By applying the sub-wavelength metallic grating, a self-polarizing THz phase shifter that achieved a phase shift of π/3 at 2 THz was reported. The operation voltage, ~130 V (rms), was still quite high.5 Meanwhile, its transmittance decreases rapidly from 80% to 10% in the frequency range of 0.2–2.0 THz.3 Recently, the phase shifter based on polymer stabilized LCs with significantly reduced response times (7 s) than devices with neat LCs was demonstrated.6 The driving voltage needed for a phase shift of 2π at 1.0 THz was ~40 V. The transmittance of this transparent device was ~17.8%. Clearly, materials serving as transparent electrodes for the THz frequency band need be developed. Indeed, a THz phase shifter utilizing graphene and LCs showed excellent transmittance.7 The maximum phase shift of this device, however, was just 10.8° at a driving voltage of 5 V.

In the visible band, indium-tin-oxide (ITO) nanomaterials, e.g., nanocolumn, nanorods (NRs), nanowires, and nanowhiskers (NWhs), with their omnidirectional, broadband anti-reflective properties, and superhydrophilicity, have been widely employed as transparent electrodes in a wide range of optoelectronic devices.12–18 In the THz band, we showed that ITO NWhs also exhibit superb transparency (~82%). Meanwhile, their DC mobility (~92 cm² V⁻¹ s⁻¹) and conductivities (~245 Ω⁻¹ cm⁻¹) are comparable to sputtered ITO thin films.19 An electrically tunable THz liquid-crystal phase shifter using ITO NWhs as transparent electrodes was proposed and demonstrated.1 Transmittance of the device was as high as ~75%. The phase shift exceeding π/2 at 1.0 THz was achieved using a ~500 μm-thick cell.1 The driving voltage required for the device operating as a quarter-wave plate was as low as 17.68 V (rms),3 an improvement of nearly an order of magnitude over previous work.3

Conventionally, homeotropic or homogeneous alignment of LC was achieved by coating or mechanically rubbing the substrate with suitable polymides (PIs), respectively. Drawbacks of the above so-called contact methods include electrostatic damage, residual stress, cosmetic defect, and dust pollution.20 Therefore, many groups pursued non-contact methods for LC alignment. Previous studies have shown that the oblique evaporation of silicon oxide (SiO₂), TiO₂, MgF₂, Al₂O₃, and metals can result in film growth in a preferred direction of LCs molecules.21–27 Later, it is shown that the pretilt angle and orientation of LC director depends on the angle of evaporation of these materials.23,26 However, few materials which can simultaneously function as transparent conductor and aligning mechanism for LC molecules have been disclosed to date.

In this Letter, we show that ITO NWhs obliquely evaporated by electron-beam glancing-angle deposition can serve simultaneously as transparent electrodes and aligned layer of LCs in a THz phase shifter. Phase shift exceeding π/2 at 1.0 THz with high transmittance (~78%) were achieved using a ~500 μm-thick LC cell. The driving voltage required for operation as a quarter-wave plate is as low as ~6 V (rms). The voltage and frequency-dependent characteristics of the THz phase shifter are discussed in detail.

Details of sample preparation by the electron-beam glancing-angle deposition (GLAD) method can be found in

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our previous work.\textsuperscript{19,28} The tilted top view and cross-sectional image of image for ITO NWhs used in this work were examined by scanning electron microscopy (SEM). These are shown in Figs. 1(a) and 1(b), respectively. A schematic illustration of the geometric relationship between the evaporation direction and director orientation of the nematic LC is presented in Fig. 1(c). The plane of incidence of THz wave is defined as the y-z plane. The angle between the z-axis (normal to the substrate) and evaporation direction, or the evaporation angle, is $\theta$. Besides, $\phi$ is the angle of inclination of the ITO NWhs from surface normal of the substrate. As a boundary condition of LC aligned by the evaporation method, the orientation of the nematic LCs is assumed to be along the x-axis, which is perpendicular to the plane of incidence of the THz wave. This is consistent with the analysis of Goodman et al.,\textsuperscript{23} who showed that orientation of LC molecules which are perpendicular to the plane of incidence (along the x-axis) requires the lowest elastic deformation energy. Therefore, it should be the preferred orientation of LCs molecules. Uchida et al. also showed that evaporation angles of SiO in the range of $70^\circ$–$80^\circ$ can reorient the LC molecules along the x-axis.\textsuperscript{26} Further, Jägemalm et al. demonstrated a surface-controlled electro-optic device by applying the SiOx to align LC in a thin LC cell (3–6 $\mu$m).\textsuperscript{29,30} With evaporated angles in the range of $67^\circ$–$75^\circ$, they claimed two uniform monostable types of alignments: the LC molecules lie in the evaporation plane with a certain pretilt for high evaporation angles and perpendicular to the evaporation plate and with zero tilt for low evaporation angles. As shown below, the alignment of LCs by ITO NWhs is consistent with these earlier works.

Transmission electron microscopy (TEM) studies revealed that the trunk of such ITO NWhs exhibits a core-shell structure, where the core is composed of crystalline $\text{In}_2\text{O}_3$ and the shell is tin-doped $\text{InO}_x$ in amorphous phase.\textsuperscript{12,14} The branches of ITO NWhs are also made of purely crystalline $\text{In}_2\text{O}_3$. We estimated the length distribution of the ITO NWhs from the SEM image. As summarized in Fig. 1(d), the height of ITO NWhs varies from 700 to 1100 nm. We estimated that the average height is 859.4 nm with a standard deviation of 108.3 nm.

The configurations of THz phase shifters studied in this work are shown in Figs. 2(a) and 2(b). The cells were constructed by sandwiching the LC (E7 by Merck) layer between two fused silica substrates that were deposited with ITO NWhs. For the phase shifters in Figs. 2(a) and 2(b), the thicknesses of the fused silica substrate and the LCs layer are $959 \pm 6$ and $517 \pm 15$ $\mu$m, versus $1008 \pm 8$ $\mu$m, and $509 \pm 12$ $\mu$m, respectively. Photoconductive (PC) antenna-based THz time-domain spectroscopy (THz-TDS) as described in our previous works were used to characterize these devices in the frequency range between 200 GHz and 1.2 THz.\textsuperscript{19,28,31,32}

The mechanisms of LC alignment for the devices in Figs. 2(a) and 2(b) are different. For the device shown in Fig. 2(b), the inner surfaces of both ITO NWhs-deposited substrates were further coated with PI alignment layers, which were lacking for the devices in Fig. 2(a). Note that these are thick cells, which are much thicker than LC cells used in optical devices. This is due to the path length requirement for phase shifting at THz frequencies.

Before undertaking the phase shifting experiments, we first checked the alignment of these LC cells by placing the cell between a pair of crossed polarizers. Dark (the director

![FIG. 1. (a) The tilted top SEM view and (b) the corresponding cross-sectional image of the ITO NWhs. (c) The schematic illustration of the geometric relationship between the evaporation direction and director orientation of the nematic LCs. (d) The height distribution of ITO NWhs as estimated from (a) and (b).](image1)

![FIG. 2. Schematic drawing of THz phase shifter (a) without PI and (b) with PI. The (c) and (d) are the dark and bright states of the THz phase shifter without PI, the (e) and (f) are the results of mechanically rubbing alignment with PI.](image2)
of LCs is parallel to one of the polarizers) and bright (the director of LCs is 45° to crossed polarizers) states for the device shown in Fig. 2(a) are shown in Figs. 2(c) and 2(d), while those for device drawn in Fig. 2(b) are presented in Figs. 2(e) and 2(f). For the device without PI (Fig. 2(b)), even though the LC layer is thick, we were able to achieve the uniform alignment (see Figs. 2(e) and 2(f)). For the device without the PI, although the alignment was not as well as that with the PI, we were still able to observe for dark and bright states (see Figs. 2(c) and 2(d)). In regard to the not so apparent dark states in both of devices, particularly the one without PI, we note that the thickness of LC cells in this work are ≥500 μm, which is ~100 times that of typical LC devices for the visible light. The ability of alignment is thus expected to be worse in the super-thick THz LC devices.

To confirm that the alignment caused by the obliquely evaporated ITO NWhs, we show the relative phase at 1.05 THz of the THz phase shifter without PI as a function of the angle, β, between LC director (x-axis) and polarization direction of the incident THz wave (see Fig. 3). The experimental data can be well-fitted by the expected sinusoid with offset of 56.93°, amplitude of 48.22°, and a period of 81.61° (maximum change of relative phase was 96.44°). The maximum and minimum of relative phases correspond to β ≈ 0° and 90°, respectively. That means the orientation of the nematic LCs must be along the x-axis, which is perpendicular to the plane of incidence. In Fig. 4, we have plotted the experimentally measured transmittance of ITO-NWhs-coated substrate, phase shifters with PI layer and LC aligned by rubbing, and that aligned by ITO NWhs only, respectively, as a function of frequency from 0.2 THz to 1.2 THz. Because of the air-space among NWhs, the transmittance of ITO NWhs (~90%) is much higher than that of sputtered ITO thin films (~8%). The THz phase shifter based on LCs aligned by ITO NWhs and rubbing exhibit similar values of transmittance, i.e., 77.8% and 75.4%, respectively.

The boundary conditions on internal surfaces of substrates for the LC cell require that the tilt angle of the director, θ(0) = θ(d) = 0, at the inner faces of the cell. Further, LC molecules are assumed to be originally aligned along the x-direction, as shown in Fig. 1. The condition for minimum free energy (δU = 0) can be written as:

\[
(k_1 \cos^2 \theta + k_3 \sin^2 \theta) \times \left( \frac{d\theta}{dz} \right)^2 - \frac{D_2^2}{(e_f/\sin^2 \theta + e_\perp \cos^2 \theta)} = \text{constants,} \tag{1}
\]

where \(k_3\), \(\theta\), \(D_2\), \(e_f\), and \(e_\perp\) are the bend elastic constant, tilt angle, the z component of the displacement field vector, the dielectric constants which are along the preferred axis and perpendicular to this axis, respectively. After assuming the maximum tilt angle, \(\theta_{\text{max}}\), at the position of \(d/2\), and defining the threshold voltage, \(V_{\text{th}} = \pi \times (k_1 e_f / (\varepsilon_0 \Delta \varepsilon))^{1/2}\), where \(e_0 = 8.854 \times 10^{-12} \text{F/m}\), \(\Delta \varepsilon = \varepsilon_f - \varepsilon_\perp = 13.8, k_1 = 11.1 \times 10^{-12} \text{N}\), and \(d\) are free-space permittivity, dielectric anisotropy, splay elastic constants, and the distance between two electrodes, respectively, the relationship between \(\theta_{\text{max}}\) and the applied voltage can be derived as:

\[
\int_0^\pi \frac{\sqrt{(1 + \zeta \sin^2 \theta_{\text{max}} \sin^2 \varphi)}}{(1 - \sin^2 \theta_{\text{max}} \sin^2 \varphi)} d\varphi \times (1 + \rho \sin^2 \theta_{\text{max}}) d\alpha = \frac{\pi V}{2 V_{\text{th}}}, \tag{2}
\]

where \(\zeta = (k_3 - k_1)/k_1\), \(\rho = (\varepsilon_f - \varepsilon_\perp)/\varepsilon_\perp\), and \(V\) is the applied voltage, whereas sin θ = sin \(\theta\)sin \(\theta_{\text{max}}\). Besides, \(V_{\text{th}}\) is the threshold voltage and equals to \(E_{\text{th}} d\). After finding the \(\theta_{\text{max}}\) at every applied voltage, the effective birefringence experienced by the THz wave transmitting through the LC cell can be written as:

\[
\Delta n_{\text{eff,Max}} = (\cos^2 \theta_{\text{max}}/n_e^2 + \sin^2 \theta_{\text{max}}/n_o^2)^{1/2} - n_{o,\perp}, \tag{3}
\]

where \(n_e\) and \(n_o\) are extraordinary and ordinary indices of refraction of the LC, respectively. Because of the ~500 μm-thick cell, we can write the phase shift due to the effective birefringence as \(\delta = 2\pi \times f \times d \times \Delta n_{\text{eff,Max}}/c\), where \(f\) and \(c\) are the frequency and speed of propagation of the THz wave in vacuum. Here, the values of \(n_e\) and \(n_o\) for E7 are 1.690–1.704 and 1.557–1.581 at 26°C, respectively, giving rise to a birefringence of 0.130–0.148 in this frequency range.
Recalling the relationship of phase shift and frequency, larger phase shift can be expected at higher frequencies. This is confirmed in Fig. 5(a), in which we have plotted the phase shifts from 0.2 to 1.2 THz as a function of the frequencies. For a given voltage, in general, the measured phase shift varied linearly with frequency. For the phase shifter in which the LC director was aligned by ITO NWhs only, the slope of linear fits varies from 10.71/THz to 91.04/THz as the applied voltage was ramped from 1.56 to 5.66 V (rms). For our previous structure, aligned by rubbing (see Fig. 2(b)),\textsuperscript{1} the slope of linear fits will vary from 7.12/THz to 92.14/THz as the applied voltage was ramped from 1.48 to 17.68 V (rms). In comparison, for quarter-wave operation, the structure in this work can be driven at much lower voltages (5.66 versus 17.68 V (rms)). The reduction is tentatively attributed to the weaker surface anchoring that is induced by the obliquely evaporated ITO NWhs.\textsuperscript{34,35} In Fig. 5(b), we plotted the phase shift as a function of driving voltage. The fitting curves in Fig. 5(b) are theoretical predictions according to (1), (2), and (3) for a given voltage, in general, the measured phase shift varies from 0.2 to 1.2 THz as a function of the frequencies. This can be attributed to the weak anchoring of the LC molecules are essentially aligned with the electric field. Here, the maximum phase shifts of theoretical curves in the different frequencies are generally in good agreements with the experiments. Meanwhile, the thresholds for voltage and electric field, $V_{th}$ and $E_{th}$ are determined to be 1.06 V (rms) and 20.50 V/cm, respectively, almost the same as the theoretically predicted values, 0.95 V (rms) and 18.32 V/cm. However, the discrepancy below $\sim$3 V (rms) is considerable. This can be attributed to the weak anchoring of the LC aligned by ITO NWhs only, which results in the reduction of operating voltages and the drastic change in the electro-optic response.\textsuperscript{35} In order to understand the level of weak anchoring on the ITO NWhs surface, further studies are required.

In summary, ITO NWhs obliquely evaporated by electron-beam glancing-angle deposition served simultaneously as transparent electrodes and aligned layer of LCs in the terahertz frequency range. To demonstrate, we constructed a THz phase shifter using the ITO NWhs. Phase shift exceeding $\pi/2$ at 1.0 THz with high transmittance ($\sim$78\%) was achieved using a $\sim$517 $\mu$m-thick LC cell. The driving voltage required for operation as a quarter-wave plate is as low as $\sim$5.66 V (rms), compatible with complementary metal-oxide-semiconductor (CMOS) and thin-film transistor (TFT) technologies.

This work was funded by the grant of the National Science Council 101-2221-E-007-103-MY3 and the Academic Top University Program of the Ministry of Education.


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**FIG. 5.** Phase shift as a function of (a) THz frequency for four driving voltages and (b) driving voltage for four frequencies of phase shifter based on ITO NWhs.
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