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Single walled carbon nano-tube, ferroelectric liquid crystal composites: Excellent diffractive tool

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We present a switchable grating based on chiral single walled carbon nano-tube (SWCNT) doped ferroelectric liquid crystals (FLCs). The presence of SWCNTs improves the diffraction profile of the pure FLC. The diffraction efficiency, i.e., the ratio of intensities of first order and zero order maxima is more than 100% for the higher concentration of SWCNTs in pure FLC. This phenomenon has been explained by the decrease in ferroelectric domain periodicity, due to the doping of SWCNTs in pure FLC, and optical activity of the chiral SWCNTs. These gratings with very high diffraction efficiency may find application in many devices. © 2011 American Institute of Physics. [doi:10.1063/1.3661170]

Tunable grating is one of the hot topics these days. Thus, liquid crystals have become attractive for applications such as diffractive optics, adaptive optics, or optical metrology.¹ While nematic liquid crystal (LC) displays are the dominant technology, devices based on ferroelectric liquid crystals (FLCs) have grown in importance because they can switch up to 100 times faster than standard nematic LCs. FLCs have found applications in diffractive optics for the generation of digital holograms,² adaptive beam steering systems,³ and polarization gratings.⁴

Recently, various LC phase gratings have been developed based on different techniques. Namely, spatially non-uniform surface treatments such as micro-rubbing and/or multiple surface treatments are sometimes necessary. Photocurable LC mixtures can make the fabrication easier,⁵ because single photo-treatment on uniformly aligned cells is enough to create patterned orientation structures, even though the fabrication procedure is complicated and expensive.

On the other hand, diffraction from surface stabilized ferroelectric liquid crystal (SSFLC) cell in the dark state can be used to make such phase gratings.^{6,7} The FLC cell, placed between crossed polarizers, diffracts light in the dark state and frustratingly decreases the display quality.^{8,9} These diffraction lobes appear only in the direction perpendicular to the alignment direction. Fig. 1 shows the intensity profile for the bright and dark states of pure FLC Felix 17/100. In fact, no diffraction exists in the bright state, whereas in the dark state, a substantially strong diffraction lobe appears. These diffraction lobes appear due to the periodicity of ferroelectric domains, and the typical periodicity of these ferroelectric domains is around $1 \sim 10 \mu\text{m}$.¹⁰ As the diffraction is limited only to the dark state, therefore, SSFLC cells can be used as tunable diffractive elements. But the diffraction efficiency of the pure FLC systems is usually very low for many applications.^{9,11}

Only the first order of diffraction appears with increasing electric field, i.e., in Fig. 1. The diffracted light intensity increases with increasing electric field; also, at the same time the intensity of main or zero order beams decreases. The diffracted beam intensity almost saturates at electric field higher than 8 V. This type of electric field dependence of intensity, of the main as well as the diffracted beams, can be explained by the simple electro-optics of liquid crystals.^{8–11} Similar dependences have also been observed for the single walled carbon nano-tubes (SWCNTs) doped FLCs that have been discussed later in the article. The first order diffraction efficiency, i.e., the ratio of intensities of first order and zero order maxima, for pure FLC is limited only up to 42%. Therefore, in pure form, FLC is not better than the existing systems.¹¹

These days, carbon nano tubes (CNTs) both single walled and multi walled are most fascinating for researchers, particularly when they are doped with the FLCs. Most of the investigations of CNTs dispersed in LCs are devoted to nematics,^{12–14} but recently, Prakash *et al.* and Podgornov *et al.* have reported improvement in response time for pure FLC due to the addition of SWCNTs.^{15,16} The dispersion of SWCNTs is also important because it possesses large surface area and π - π surface electron that results in strong electrostatic interaction between the SWCNTs and surrounding medium. In addition to this, SWCNTs can be of different types depending on the so-called chiral vector (n,m). The SWCNTs having $n=m$ (chiral angle = 0°) are known as armchair and those with $m=0$ (chiral angle = 30°) are zigzag; otherwise they are chiral nano tubes.¹⁷ The SSFLC cells are phase grating, thus chiral SWCNTs can be used to improve the diffraction profile of pure FLCs.¹⁸ The typical size of liquid crystal molecules and layers is around $5 \sim 100 \text{ nm}$,⁸ therefore, chiral SWCNTs of sizes 100 nm in length and 3 nm in diameter have been doped in pure FLC Felix 17/100 in concentrations of 0.25% and 0.5% wt/wt. The basic parameters of FLC Felix 17/100 are spontaneous polarization is 47 nC/cm^2 , tilt cone is 55.1° , and optical

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FIG. 1. (Color online) The intensity profile of the bright as well as the dark states for the Pure FLC Felix 17/100 at electric field of 14 V. Left insertions represent the photographs for bright and dark state, while the right insertion shows the intensity profile of dark state at different electric field.

anisotropy is 0.172. The proper dispersion of SWCNTs in FLC matrix has been insured by agitating the vial containing the mixture just below the isotropic transition temperature of FLC. The $1.5\ \mu\text{m}$ thick planar aligned SSFLC cells have been prepared by coating $10\sim 20\ \text{nm}$ thick Nylon 6/6 alignment layer on ITO coated glass substrates. The diffraction patterns have been studied by placing cells between the crossed polarizers and mounting them with one of the tilt positions parallel with the polarizer axis. Just after the analyzer, a screen has been placed to see the diffraction pattern. Cells have been illuminated by He-Ne laser at room temperature, and diffraction patterns have been captured by the digital camera in bright as well as dark states at different applied electric fields. Afterwards, MATLAB was used to analyze the intensity profile.

Interestingly, the diffraction profile improves much as we add SWCNTs in FLC (Fig. 2), and higher orders of diffraction lobes also appear for highly concentrated cells. Intensity of diffracted beam increases particularly for the first order, also the position of maxima shifts. The shift in the position of maxima suggests increase in the diffraction angle, which means that after doping SWCNTs in FLC the period of the structure is decreased. The period for pure FLC is $4.1\ \mu\text{m}$; whereas for 0.25% and 0.5% SWCNTs doped FLC, it becomes $3.42\ \mu\text{m}$ and $2.93\ \mu\text{m}$, respectively. This decrease in the period is due to the interaction between SWCNTs and FLC matrix that increases spontaneous polarization of the composite,¹⁹ consequently the period decreases.¹⁰ As the intensity of diffracted beam increases for SWCNTs doped FLC in comparison to pure FLC, it is important to study the diffraction efficiency as a function of applied electric field (Fig. 3).

As expected, the diffraction efficiency for pure FLC increases at the higher electric field and almost saturates after 11 V: the maximum diffraction efficiency for pure FLC is less than 45%. Qualitatively the diffraction efficiency for

FIG. 2. (Color online) The dark state intensity profile of the pure and SWCNTs doped FLC at electric field of 14 V. Insertions show photographs of diffraction lobes for (a) pure FLC Felix 17/100, (b) 0.25% SWCNTs doped FLC, and (c) 0.5% SWCNTs doped FLC. The marker size in the photographs (a) and (b) is 1 cm, while for (c), it is 3 cm.

SWCNTs doped FLC, as a function of electric field is the same, but quantitatively it is considerably better than pure FLC. Diffraction efficiency for 0.25% and 0.5% SWCNTs doped FLC, at electric field of 14 V, is around 56% and 120%, respectively. This enormous increase in diffraction efficiency for 0.5% SWCNTs doped FLC is of great interest for several applications particularly for beam steering devices, optically addressed SLMs (OASLMs) and other adaptive optic elements.¹¹ In the next section, we give the explanation for this huge increment in diffraction efficiency for doped FLC.

The Intensity of different diffraction orders for FLC grating can be written as²⁰

$$S(f) = |a_{AD}e^{i\delta_D}e^{-j\pi f a}\text{Sinc}(af) + (b-a)A_Ue^{i\delta_D}e^{-j\pi f(a+b)} \times \text{Sinc}\{(b-a)f\}|^2$$

FIG. 3. Electric field dependence of the first order diffraction efficiency for pure and SWCNTs doped FLCs. Inset shows the variation of transmittance of all cells at different analyzer angles.

here f is the order of diffraction, a , b are the thickness and period of ferroelectric domain, respectively, while δ_U and δ_D represents the phase difference generated by two different ferroelectric domains. The amplitude and phase are, respectively, A_D and $\delta_+ + \delta_D$ in one domain and A_U and $\delta_+ + \delta_D$ in other domain.

Therefore, the first order diffraction efficiency can be written as:

$$\frac{S(1)}{S(0)} = \frac{q^2 \text{Sinc}^2(a) |A_D - A_U e^{j(\delta_u - \delta_d)}|^2}{|qA_D + (1-q)A_U e^{j(\delta_u - \delta_d)}|^2} \times 100; \quad q = a/b. \quad (1)$$

From here one may conclude that the decrease in the period, due to addition of SWCNTs in pure FLC matrix, could be attributed to the high diffraction efficiency. However, the period for 0.5% SWCNT doped FLC, compared to the period for the pure FLC, only decreases by 29%, which can increase the diffraction efficiency only up to 59%, whereas it is more than 120%. Therefore, the decrease in the period is not only responsible for this vast increment in diffraction efficiency, but the optical activity of the nano tube also plays a crucial role.^{21,22} To confirm this, the optical transmittance of cells for the main beam has been measured with rotating analyzer, by keeping the LC alignment direction parallel to the polarizer (inset, Fig. 3). It is clear from the figure that optical activity of SWCNTs strongly contributes. Thus, the optically active SWCNTs introduce some excess phase in the plane of polarization of diffracted light. Therefore, after passing through the analyzer, the intensity of the diffracted light is much more than it was expected. This excess phase in the diffracted beams increases at the higher concentrations of SWCNTs. As a consequence, the diffraction efficiency increases more than 100% for 0.5% SWCNTs doped FLC. Therefore, both optical activity of SWCNTs and decrease in the period are responsible for such a huge increment in diffraction efficiency.

In summary, we have analyzed the diffraction profile of the pure and SWCNTs doped FLC. No diffraction exists in the bright state, while clear diffraction lobes were observed in the dark state. Therefore, these structures can be used as tunable grating and beam steering devices. The first order diffraction efficiency increases with the addition of SWCNTs in pure FLC matrix and becomes more than 100% for 0.5% SWCNTs doped FLC. This increase in diffraction efficiency has been explained on the basis of decrease in ferroelectric domain periodicity and optical activity of the SWCNTs. As the

diffraction is only limited to the dark state of SSFLC, and thus the light transmission may be an issue; but the optimization of FLCs, SWCNTs, and cell parameters can solve it. Typically, the switching time of these samples is less than 200 μ s. Thus, SWCNTs doped FLC, with high diffraction efficiency, has extreme potential for application in many devices, e.g., tunable diffraction grating, OASLMs and other adaptive optic elements like optical Interconnect. It is also advised to use optimum concentration of SWCNTs in FLC to avoid the percolating behavior of the electrical conductivity (σ).¹⁹ Otherwise, σ of the system may increase enormously.

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