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Flexible, ferroelectric nanoparticle doped polymer dispersed liquid crystal devices for lower switching voltage and nanoenergy generation

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ABSTRACT

Flexible polymer dispersed liquid crystal (F-PDLC) devices were fabricated using transparent conducting ITO/PET film. Polymerization induced phase separation (PIPS) method was used for pure and ferroelectric $BaTiO_3$ (BTO) and ZnO doped PDLC devices. The distribution of nanoparticles in the PDLC and the formation of micro cavities were studied using field emission scanning electron microscopy (FESEM). It was observed that the addition of ferroelectric BTO nanoparticles has reduced the threshold voltage (V_{th}) and saturation voltage (V_{sat}) of F_{NP}-PDLC by 85% and 41% respectively due to the spontaneous polarization of ferroelectric nanoparticles. The ferroelectric properties of BTO and ZnO in the fabricated devices were investigated using dynamic contact electrostatic force microscopy (DC EFM). Flexing the device can generate a potential due to the piezo-tribo electric effect of the ferroelectric nanomaterial doped in the PDLC matrix, which could be utilized as an energy generating system. The switching voltage after multiple flexing was also studied and found to be in par with non-flexing situations.

1. Introduction

In recent years, research on electro-optical devices gained a lot of attention, due to its low power consumption and aesthetics. Among which, most of the works were concentrated on the liquid crystals; a magic liquid which exhibits an orientational order as in crystals, with an optical anisotropy [1]. This property was being explored in developing liquid crystal devices; to mention a few are twisted nematic liquid crystal devises, in plane switching devices, switchable windows etc. The devices based on this mesogenic material are of great demand, because of its light weight, flexibility, compatibility and low power consumption [2,3]. Among the different kinds of liquid crystal devices, polymer dispersed liquid crystal (PDLC) devices have been the subject of both academic research and industrial application. This device consists of a polymer matrix in which the liquid crystals are trapped as micro droplets [4–6]. The micro droplets formed acts as domain which exhibits the orientational ordering of crystals, controlled by an applied electric field. Transition from a high light scattering state (OFF) to a transparent state (ON) could be achieved by the application of an AC field. The transmittance can be tuned by adjusting the field applied, thus act as an optical shutter [5]. For conventional system the anchoring force between the liquid crystal droplets and polymer matrix is higher thus a large voltage is required to align the molecule [7]. To resolve this problem inorganic nanoparticles such as SiO_2, ZnO, CuO are being introduced into the polymer system [8–10]. Active research is going on to lower the power consumption of these devices to make it more energy efficient [11]. Embedding of ferroelectric nanoparticles in the PDLC devices resulted in reduction in the switching voltage of the device. Ferroelectric nanoparticles within the liquid crystal shows an enhancement in dielectric properties, spontaneous polarization and further improve the electro optical property [12,13]. Ferroelectric nanoparticles are being trapped in the micro droplet of liquid crystal as sub domain. Remanent polarization of ferroelectric nanoparticles can effectively influence the alignment of liquid crystal molecules in the polymer matrix, thereby reducing the switching voltage as well as the response time of the PDLC devices [14]. Moreover flexibility for the device is a necessity when it comes to their integration to the optical/optoelectronic devices in the present day life. The flexibility of these devices is achieved by introducing flexible conductive electrodes like ITO/PET or Graphene/PET [15,16]. There are no reports on flexible ferroelectric nanoparticle doped PDLC device with piezo-tribo nanoenergy harvesting. In this work ferroelectric nanoparticles (BTO, ZnO) are doped into a flexible PDLC device and its electro-optical behaviors are studied. The ferroelectric nature of the PDLC system was studied by the DC EFM and its piezo-trio electric effect was investigated using digital oscilloscope. Interfacial polarization occurring at the polymer nanoparticle interface can attain high dielectric constant and low dissipation factor, which can be reflected on to the capacitance of the

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device [17,18]. Morphology and size of the nanoparticles in the active layer can also influence the capacitance of the device [19].

2. Experimental section

Liquid crystal, E7 (+ε, refractive index-n_o = 1.5216, n_e = 1.7462 at λ = 589 nm, 20 °C) [10] was purchased from Merck, Darmstadt, Germany, which is a combination of four different cyanobiphenyls. Polymer matrix used was NOA 65 (n = 1.524 at λ = 633 nm, 30 °C) [20] Norland, USA. $BaTiO_3$ (BTO) (30–50 nm) and ZnO (60–80 nm) nanoparticles were purchased from Sigma Aldrich and used obtained. Liquid crystal (LC) and the polymer were taken in 1:1 ratio, and mixed well using a probe sonicator (Sonics Vibra cell) for 1 min at 150 W. Then mixtures were filled inside an indium tin oxide (ITO) coated flexible PET cell (3 cm × 3 cm) with 50 μm spacer, by capillary action. The cells were cured under UV light (384 nm) for 15 min at 160 W and the same was used as a reference cell. PDLC devices were also fabricated using ferroelectric BTO and ZnO nanoparticles by mixing with the polymer/LC mixture. To obtain a uniform dispersion of nanoparticles, the solution (polymer-LC mixture and nanoparticles) were probe sonicated for 60 s. This process was repeated at regular intervals with the assistance of water bath maintaining a temperature of 25 °C. Morphology of fabricated PDLC film was characterized using field emission scanning electron microscopy (FESEM, Hitachi, SU 6600, Japan). Dynamic contact electrostatic field microscopy (DC EFM) studies were done using atomic force microscopy (Park XE 100) in tapping mode over a scan area of 5 μm × 5 μm at a scanning rate of 1 Hz using a NSC14-Cr/Au tip. A lock in amplifier (Stanford research system, SR830) was used to modulate the conducting tip at an alternating voltage of 3 V and a frequency of 16 kHz. The transmission –voltage characteristics was measured and compared with the reference cell. For this, a setup consists of a diode laser (wavelength-532 nm, 5 mW, Holmarc), Si based photo detector (Thorlabs) and a variable AC supply (Keysight, AC6801A) was employed, as depicted in Fig. 1. The capacitance of the fabricated devices was measured using an impedance analyzer (Wayne Kerr 6500B precision Impedance Analyzer). Voltage measurement during flexing was carried out using a digital storage oscilloscope (Agilent Infiniti 200×).

3. Result and discussion

Fig. 2 shows the transmission electron microscopy (TEM) images of the ferroelectric BTO and ZnO nanoparticles used in the fabrication of F_{NP}-PDLC devices. The BTO nanoparticles have a size ranging from 30 to 50 nm and ZnO nanoparticle with a size of 60–80 nm.

Light scattering and light transmitting ability of the PDLC is due to the formation of the liquid crystal micro droplets in the polymer matrix. The formation of these micro droplets was studied using FESEM. The formations of micro cavities were observed both in the case of pure and doped devices. These micro droplets act as domains, with each domains trapping the ferroelectric nanoparticles and leads to the formation of a subdomains. Ferroelectric nanoparticles can get trapped both in the LC as well as in the polymer matrix while doping. As the doping concentration of the nanoparticles increases, agglomeration in the polymer matrix was observed and resulted in the reduction of transmittance. The concentration of ferroelectric nanoparticles was optimized to 0.8 wt% based on the electro-optical measurements, which is discussed in the later section. Fig. 3(a) and (d) shows the FESEM images of BTO and ZnO nanoparticles respectively. Highly agglomerated spherical particles are observed in the case of BTO and a rod like morphology was observed in the case of ZnO nanoparticles. Fig. 3(b) and (e) shows FESEM images of the micro cavities in the PDLC material after removing the liquid crystal. From these figure it is clear that there is uniform dispersion of nanoparticle in the polymer matrix for 0.8 wt% BTO and 0.8 wt% ZnO doped PDLC which are present inside and outside the micro cavities. At higher concentrations (> 1 wt%), the both BTO and ZnO doped PDLC materials exhibit agglomeration, as shown in Fig. 3(c) and (f). This leads to a reduction in the transmittance.

Fig. 4 shows the transmittance-voltage curve of pure and ferroelectric nanoparticle doped F-PDLC devices. The curve was recorded by sweeping the AC voltages at 50 Hz using the electro-optical setup. The BTO doped F-PDLC shows a steep curve from OFF state to ON state, with a lower threshold and saturation voltage of 5 V and 40 V respectively. It can be observed that a reduction in switching voltage for BTO doped device, when compared with ZnO doped and pure PDLC device. A lower switching time can be expected while observing the steepening of the curve for BTO doped devices. A reduction in optical transmittance was observed with the doping of nanoparticles. Switching time of the devices at different concentrations (0.2, 0.4 0.6, 0.8 and 1 wt%) were investigated for both ZnO and BTO doped PDLC devices as shown in Fig. 5(a and b). It can be observed that in both cases the switching time decrease with nanoparticle concentration due to the increased polarization of the ferroelectric nanoparticles and their interaction with liquid crystal molecules. Based on this study the concentration of the nanoparticle in the F_{NP}-PDLC was optimized to be 0.8 wt%.

The enhancement of this electro-optical property is due to the local electric field produced inside the sub domains of the device. When compared to the pure F-PDLC device, the ferroelectric nanoparticles doped F_{NP}-PDLC produces a local electric field and aligns the LC molecules in the direction of the field. The switching behavior of the devices even after multiple flexing upto an angle of 80° was studied and is shown in Fig. 6. Photograph of fabricated flexible BTO doped PDLC in the ON and OFF state at an angle of 60° is shown in Fig. 7.

The ferroelectric property of PDLC was studied using the DC EFM on a spin coated sample. The studies show that BTO doped devices exhibit an enhanced ferroelectric property compared to that of the pure sample. The butterfly loop obtained from the voltage amplitude curve of DC EFM gives the extent of ferroelectric nature of doped devices [21]. A classical butterfly loop was obtained for BTO doped device when applied bias is varied from 0 to 10 V. This behavior is due to the field induced alignment of the ferroelectric subdomains in the device. As we decrease the applied voltage from 10 V to 0 V, amplitude retraces a different path due to the remanent polarization of the doped nanoparticle resulting in a hysteresis loop as shown in Fig. 8(d and e) for concentration of 0.8 wt% and 1 wt%. This effect is directly reflected on to the switching voltage of the BTO doped device. When comparing with ZnO doped device, the extent of polarization is less, with negligible loop opening, even at a sample bias of −10 to +10 and is shown in Fig. 8(b and c) for 0.8 wt% and 1 wt%. Pure PDLC does not show any characteristic hysteresis loop which proves that the device is non-ferroelectric in nature Fig. 8(a).

The phase response obtained from DC EFM for pure and doped device are shown in Fig. 9. Pure PDLC does not show any characteristics curve as shown in Fig. 9(a). Polarization reversibility was found for

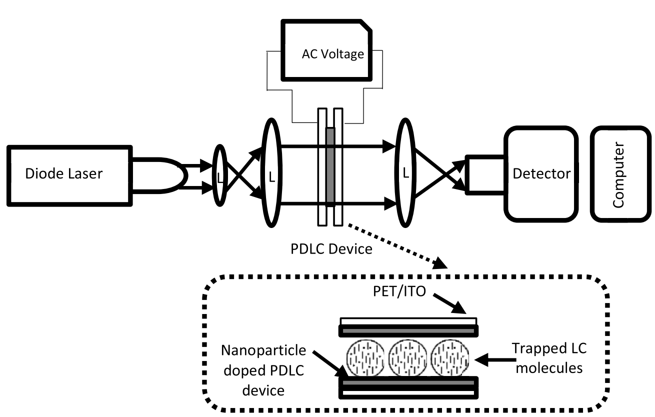

Fig. 1. Schematic diagram for the electro optical setup employed for the characterization of the F- PDLC devices.

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