Strong charge trapping and bistable electrowetting on nanocomposite fluoropolymer:$BaTiO_3$ dielectrics

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Strong charge trapping and bistable electrowetting on nanocomposite fluoropolymer:$BaTiO_3$ dielectrics are reported. Thin nanocomposite dielectrics were spin casted from $BaTiO_3$ nanopowder dispersed in a fluoropolymer/fluorosolvent solution. Electrowetting contact angle versus voltage and capacitance measurements confirm a severalfold increase in film dielectric constant with increasing $BaTiO_3$ content. Bistable electrowetting was observed as droplets retained a decreased contact angle at 0 V but would dewet the surface by briefly applying a reverse polarity voltage. Strong charge trapping in the nanocomposite was confirmed by charge-voltage hysteresis. These results could prove important for low-power applications such as bistable displays and electronic paper.
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Electrowetting[1] continues to experience rapid growth in applications including digital laboratory-on-chip,[2,3] high-efficiency displays,[4,5] and liquid optics.[6,7] Conventional electrowetting of a liquid droplet is performed on an electrode covered by an approximately micrometer thick film of hydrophobic fluoropolymer. Applying voltage between the droplet and electrode causes electrowetting and is macroscopically observed by a decrease of the contact angle of the droplet. Submillimeter scale droplet devices show rapid (approximately milliseconds) reversibility of wetting as the voltage is applied/removed. Electrowetting behavior can be predicted by the so-called electrowetting equation

$$\cos(\theta_V) = \cos(\theta_Y) + \frac{1}{2}\frac{\varepsilon V^2}{\gamma z}, \tag{1}$$

where θ_Y is Young's contact angle determined by interfacial surface tensions at zero applied voltage, θ_V is the electrowetted contact angle at an electrical potential of V, ε is the electric permittivity of the dielectric layer beneath the droplet, γ is the liquid/air or liquid/oil interfacial surface tension, and z is the thickness of dielectric layer.

Two observations can be readily made from Eq. (1). First, if a higher permittivity fluoropolymer could be developed it would reduce the voltage required for electrowetting. Second, as long as the liquid/fluoropolymer/electrode capacitor retains charge the droplet will remain electrowetted without further power consumption. Reported here is a nanocomposite fluoropolymer:$BaTiO_3$ dielectric approach that provides higher capacitance and therefore a decreased electrowetting voltage. It has also been demonstrated that, at higher $BaTiO_3$ contents, the nanocomposite dielectric shows very strong charge storage/trapping behavior and bistable electrowetting (Fig. 1). These findings are reported along with a simple means of measuring the voltage and time-dependent stored charge in an electrowetting device.

The nanocomposite dielectric was prepared by dispersing $BaTiO_3$ nanopowder (HPB-1000, TPL Inc.,) in an electrowetting-capable fluoropolymer such as DuPont Teflon AF or Asahi Cytop ($\gamma < 20$ mN/m). The $BaTiO_3$ nanopowder has a mean particle size of 56 nm and a spherical morphology. The $BaTiO_3$ nanopowder has a cubic crystal structure and a dielectric constant of $\varepsilon_r \sim 200$ which is two orders of magnitude greater than the $\varepsilon_r \sim 2$ for the fluoropolymer. $BaTiO_3$ was dispersed in fluorosilane (IT CFB 3958, Dow Corning) and fluorosolvent by ultrasonication for 30 min. A

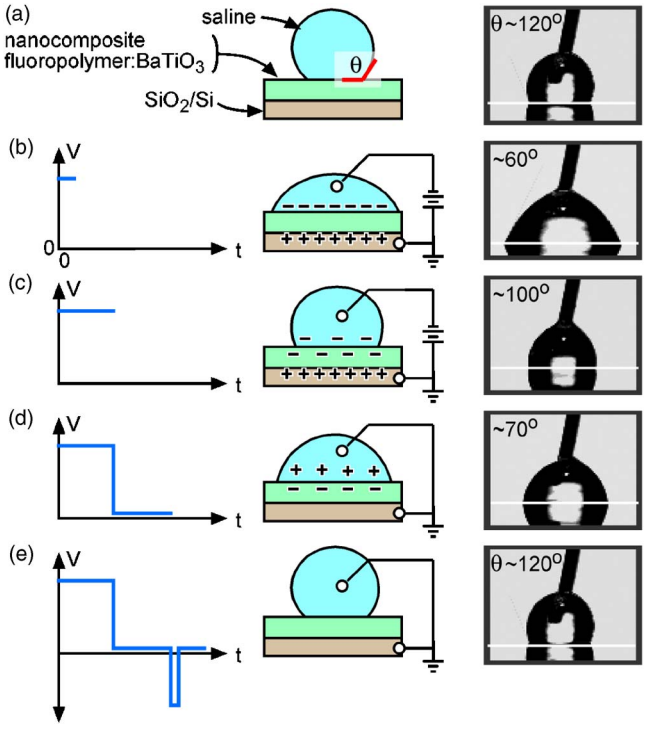


FIG. 1. (Color online) Qualitative diagrams and photographs of electrowetting droplet measurements on nanocomposite fluoropolymer:$BaTiO_3$ films. The voltage vs. time and qualitative representation of charge storage are shown to aid in understanding of the bistable electrowetting effect.

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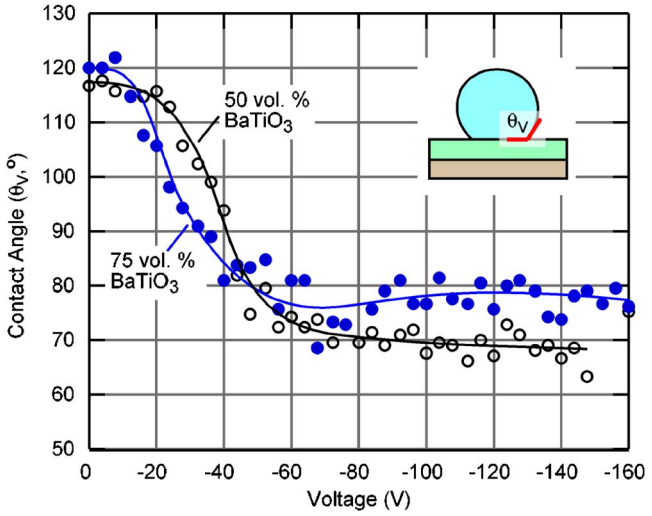


FIG. 2. (Color online) Electrowetting contact angle vs. voltage for 1.0 μm of nanocomposite with ~50 vol % $BaTiO_3$ (black line) and 1.2 μm of nanocomposite with ~75 vol % $BaTiO_3$ (blue line).

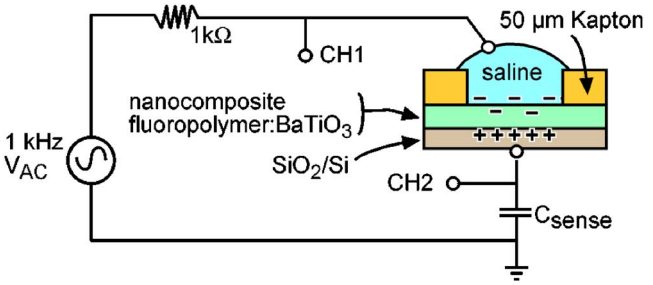


FIG. 3. (Color online) Capacitance vs. voltage measurement setup including oscilloscope channel leads. In order to maintain constant area for the saline/nanocomposite/Si capacitor, a 50 μm thick Kapton™ grid limits the contacting droplet area.

desired volume of fluoropolymer/fluorosolvent solution is then added to the suspension to obtain various fluoropolymer:$BaTiO_3$ compositions by vol %. These suspensions were found to be stable for at least several days. Test samples were prepared by spin coating the nanocomposite dielectric onto a silicon wafer with a thermal oxide thickness of 100 nm. The nanocomposite films are first allowed to air dry to maximize the film density. Following the air dry, the approximately micrometer films are oven baked at 160 °C for 30 min. The thin thermal oxide is not absolutely necessary, but it improves the fabrication yield by preventing electrolysis at any pinholes/defects in the nanocomposite dielectric film. Initial tests revealed that the stand-alone nanocomposite film exhibited large surface roughness and contact angle hysteresis for $BaTiO_3$ content greater than 25% by volume. Furthermore, the fluorosilane dispersant reached the surface of the cured films and increased the observed surface energy to >20 mN/m. In order to obtain a smoother and more hydrophobic surface, a ~200 nm top coat of pure fluoropolymer/fluorosolvent solution was added to each sample and rapidly baked to minimize dissolution of the underlying nanocomposite fluoropolymer. Process parameters for both the nanocomposite films and pure fluoropolymer top coat were modified for each fluoropolymer:$BaTiO_3$ composition in order to keep the total dielectric film thickness between ~0.8 and ~1.2 μm. Capacitance measurements on completed samples revealed that the measured (average) dielectric constant of the nanocomposite films increased from ~2 to >10 as $BaTiO_3$ content was increased to >75% by volume.

Electrowetting contact angle versus voltage was measured by stepping the applied voltage at 4 V/s and by capturing the image of the saline droplet (0.1*M* KCl) after each voltage step. Typical electrowetting results for the 50 and 75 vol % samples are shown in Fig. 2. The 50 and 75 vol % samples exhibited the most rapid change in contact angle versus voltage whereas the 25 vol % sample (not shown) exhibited little difference compared to a pure fluoropolymer sample. For all samples, as $BaTiO_3$ vol % was increased, the onset of contact angle saturation occurred at lower voltages. Early onset of saturation is due to charge injection into the nanocomposite film and will be further understood via the discussion in the next sections. The ~1 μm thick 50 and 75 vol % samples exhibited electrowetting behavior comparable to an ~0.5 μm thick film of pure fluoropolymer film. This is due to an approximate doubling of dielectric constant for the nanocomposite films as compared to a pure fluoropolymer film [Eq. (1)].

Turning our attention to Fig. 1, the observation of bistable electrowetting can be qualitatively explained as follows. At zero bias the droplet rests at Young's angle [Fig. 1(a)]. Upon application of voltage the droplet electrowets the surface as charge accumulates near the saline/nanocomposite interface [Fig. 1(b)]. The droplet is then held at the voltage corresponding to contact angle saturation. At contact angle saturation charge injects into the nanocomposite film [Fig. 1(c)], an effect observed in electrowetting on conventional fluoropolymers as well.[8] The dielectric constant and nonplanar morphology of the $BaTiO_3$ particles should locally increase the electric field dropped across the fluoropolymer phase. This should increase the charge injection and screen the charge that would otherwise accumulate near the saline/nanocomposite interface. As a result of this increased charge injection and screening, the droplet dewets the surface. The saline is then grounded and the injected/trapped charge causes a reverse polarity charge accumulation near the saline/nanocomposite interface. This causes the droplet to once again electrowet the surface [Fig. 1(d)]. Stable wetting in the state of Fig. 1(d) could be achieved for several minutes. It was further observed that trapped charge could be removed and the droplet dewetted by applying a short (approximately milliseconds) reverse polarity voltage pulse [Fig. 1(e)]. This switching between various wetting states without need for constant voltage application provides bistability. It is important to note that no materials optimization was performed to either increase or decrease the magnitude or stability of injected/stored charge. Therefore, future work is likely to provide greatly improved bistability. It is also important to note that charge injection and dewetting were also observed for thin (<0.2 μm) fluoropolymer films formed on sputter-deposited $BaTiO_3$ thin films. However, these devices did not exhibit strong trapping behavior (i.e., stable wetting states).

Charge-voltage (*Q-V*) analysis was performed to further correlate charge trapping with increasing $BaTiO_3$ content. A diagram of the *Q-V* sensing circuit is shown in Fig. 3. *Q-V* analysis using the Sawyer-Tower circuit[9] has been utilized extensively for characterizing charge trapping in high-field inorganic electroluminescent devices.[10,11] As shown in Fig. 3, a droplet is placed over an aperture in a 50 μm thick

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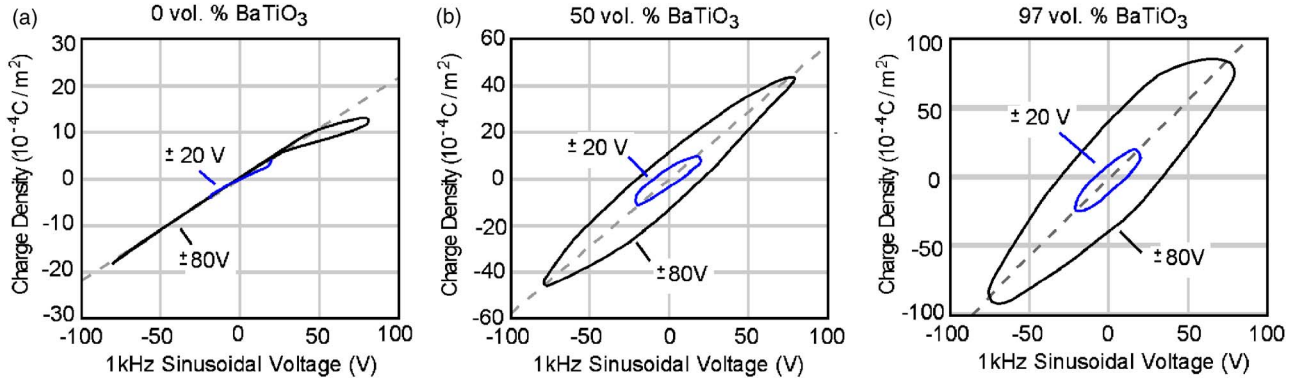


FIG. 4. (Color online) Charge-voltage analysis at +/−20 and +−80 V_p 1 kHz sinusoidal voltage for the minimum through maximum achievable $BaTiO_3$ content in the nanocomposite film. The 97 vol % $BaTiO_3$ is the specification for the original as deposited $BaTiO_3$/fluoropolymer ratio and is larger than the actual vol % of $BaTiO_3$ after the pure fluoropolymer top coat is added.

DuPont Kapton tape film. The Kapton limits the saline electrode (capacitor) area since otherwise the saline electrode area would vary as the droplet electrowets the nanocomposite film. Sinusoidal voltages (1 kHz) were applied to the sample. Both ±20 and ±80 V_p curves were plotted. The circuit is probed (CH1, CH2, Fig. 3) and fed into an oscilloscope operating in *XY* mode and data averaging. *Q-V* results for 0, 50, and 97 vol % $BaTiO_3$ content are plotted in Fig. 4. It is important to note that the vol % represents the original as-deposited $BaTiO_3$/fluopolymer ratio. The application of the pure fluoropolymer top coat is expected to fill numerous voids in the 97% $BaTiO_3$ film. Therefore, the true vol % of $BaTiO_3$ should be substantially lower than 97%. However, the purpose of these plots is simply to provide *Q-V* measurement for the minimum through maximum $BaTiO_3$ content achievable with the fabrication process utilized herein.

Referring to Fig. 4(a), the *Q-V* plot for no $BaTiO_3$ content exhibits behavior similar to an ideal capacitor (dashed gray line) for both the 20 and 80 V curves. At large positive voltage, the slight hysteresis and dip below the ideal capacitor trend is not fully understood at this time, but may be due to electrical breakdown of the fluoropolymer. Observation of an earlier onset of breakdown for positive saline voltage is consistent with our electrowetting tests on thin fluoropolymer films. Polarity dependent breakdown voltages have also been previously reported for Teflon AF films.[12] As $BaTiO_3$ content is increased [Figs. 4(b) and 4(c)] there is a clear increase in the *Q-V* hysteresis. This provides direct evidence of strong charge injection and trapping. As expected, the hysteresis also increases as the applied voltage increases from 20 to 80 V. Zero charge occurs only as a substantial reverse polarity is applied. This is consistent with the ability to dewet the bistable droplet wetting with a brief reverse polarity voltage pulse. Increasing charge injection with increasing $BaTiO_3$ is also consistent with the earlier onset of electrowetting saturation observed in Fig. 2. The *Q-V* curves are not as well behaved as the *Q-V* for inorganic electroluminescent devices.[10,11] This is not unexpected since trap location (distance from surface) and trap depth (eV) are likely much more homogenous in multilayer thin film devices.

Contribution to the observed hysteresis by the ferroelectric nature of the $BaTiO_3$ particles[13] should also be considered. The $BaTiO_3$ has a mean particle size of 56 nm and is primarily cubic. Although some tetragonal structure has been reported for particles at this scale, the degree of ferroelectricity is likely too small to explain the strong *Q-V* hysteresis and bistable electrowetting reported in this work. Furthermore, the shape of the hysteresis curve more closely resembles that expected for charge trapping[10,11] than that expected for ferroelectric behavior. Also, the electric field across the $\varepsilon_r \sim 200$ $BaTiO_3$ particles embedded in $\varepsilon_r \sim 2$ fluoropolymer is not substantially large. It is therefore concluded that charge trapping, not ferroelectricity, dominates the *Q-V* hysteresis. Future work may investigate the ferroelectric contribution in more detail, or even utilize larger size $BaTiO_3$ particles to purposely obtain composite electrowetting dielectrics that exhibit strong ferroelectric behavior. Some speculation on the location of charge trapping and on possible applications is provided. The unterminated bonds at the surface of the $BaTiO_3$ are possible charge storage centers. In future work, one may consider creating more homogenous trapping centers by coating the $BaTiO_3$ with a thin second dielectric such as ZnS.[10,11] The dispersant and particle size could also be sources of optimization. This would allow one to engineer the trap depth (eV), density, and stability. Optimized charge trapping in nanocomposite hydrophobic dielectrics could provide technologically important results such as reduced power consumption for applications such as electronic paper or reflective displays.[4] For example, bistable switching would allow devices to be electrically refreshed only every few minutes, hence providing significant power savings.

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