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Doped polymer electrodes for high performance ferroelectric capacitors on plastic substrates

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Flexible ferroelectric capacitors with doped polymer electrodes have been fabricated on plastic substrates with performance as good as metal electrodes. The effect of doping on the morphology of polymer electrodes and its impact on device performance have been studied. Improved fatigue characteristics using doped and undoped poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) electrodes versus metal electrodes are observed. It is shown that the polymer electrodes follow classical ferroelectric and dielectric responses, including series resistance effects. The improved device characteristics obtained using highly conducting doped PEDOT:PSS suggest that it may be used both as an electrode and as global interconnect for all-polymer transparent circuits on flexible substrates. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4757426]

Organic electronics targeting next generation transparent and flexible electronics applications continues to be heavily investigated. An integral part of most flexible electronic circuits is a non-volatile memory component, preferably transparent, that can be used to store and retrieve information as required. Traditional memory circuits based on silicon technology are difficult to integrate with flexible and transparent plastic substrates due to the required high-temperature processing and limited flexibility of silicon. These problems can be overcome by using polymer ferroelectric memories. A promising candidate material is poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) due to its transparency, non-volatility, large spontaneous polarization, excellent chemical stability, and low temperature processability.1–3 Moreover, the use of easily patternable, spin-cast films of conducting polymer electrodes opens the possibility of large scale fabrication of flexible and transparent ferroelectric memory. The use of polymer electrodes presents unique challenges for the fabrication of electronic devices. In contrast to metal electrodes, the morphology and processing conditions of these conducting polymer electrodes can affect their properties and the electronic devices made thereof. There have been limited reports on the use of conducting polymers as electrodes and interfacial layers for ferroelectric capacitors.4,6 but there are no studies reporting on how the morphology and conductivity of the underlying polymer electrodes affect the dielectric and ferroelectric properties of the memory devices.

A variety of polymers such as polypyrrole, polyaniline, and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) offer a unique combination of properties that make them attractive for transparent electronics. These polymers are made conducting by the reaction of the conjugated semiconducting polymer with an oxidizing agent, a reducing agent, or a protonic acid. The conductivity of these materials can be modified by the nature and degree of doping.7 The easily tunable optical, chemical, and electrical properties of PEDOT:PSS make it the most widely used conducting polymer for numerous applications such as organic light-emitting diodes (OLEDs), organic photovoltaic (OPVs), organic thin film transistors (OTFTs), and hybrid nanocomposites for thermoelectrics.8–10 In this study, we analyze and compare the performance and reliability of capacitors fabricated using doped/undoped PEDOT:PSS polymer electrodes to metal electrodes. The device performance is characterized using polarization–electric field (P–E) curves, capacitance–voltage (C–V) curves, dielectric spectroscopy, and fatigue analysis.

High performance thermoplastic polyetherimide sheets (Ultem 1000B) supplied by Saudi Basic Industries Corporation (SABIC) were used as the substrate. Prior to device fabrication, the substrates were cleaned by ultra-sonication in acetone, isopropanol and de-ionized water. To study the effect of series resistance from polymer electrodes in a metal-ferroelectric-metal device architecture, a broad range of conductivity is essential, and hence PEDOT:PSS from Sigma Aldrich was used without modification with a conductivity of ~1 S/cm. In contrast, PEDOT:PSS in the form of Clevios PH-1000 from Heraeus was chemically doped to control its conductivity. We found that a maximum conductivity of ~915 S/cm could be achieved by doping the PH-1000 with ~4 wt.% dimethylsulfoxide (DMSO). The thickness, sheet resistance, and conductivity of spin-cast films of different kinds of PEDOT:PSS used in this study are summarized in Table 1. The thicknesses were measured using a Dektak profilometer, and the sheet resistance values were measured with a 4-point probe system. The inherently hydrophobic polyetherimide substrates were treated with O2 plasma for 2 min, rendering the surface hydrophilic, essential
for spin-casting uniform, thin films. Bottom electrodes were formed by spinning the PEDOT:PSS solutions at 1500 rpm for 30 s, followed by annealing on a hotplate at 120 °C for 30 min. A 2 wt. % solution of P(VDF-TrFE) (70–30 mol. %) dissolved in methylethylketone (MEK) was then spun on the PEDOT:PSS film at 3000 rpm for 60 s, followed by a soft bake for 30 min at 80 °C. The films were then annealed in vacuum at 135 °C for 4 h to improve the crystallinity and obtain the ferroelectric phase. The P(VDF-TrFE) layer was 120 ± 5 nm thick, as measured by a Dektak profilometer. Gold (Au) was thermally evaporated through a shadow mask to define the top electrodes. For comparison, a capacitor with Au and Pt as top and bottom electrodes, respectively, was also made with the same P(VDF-TrFE) thickness. Different bottom electrodes of platinum, undoped PEDOT:PSS, and doped PEDOT:PSS are referred to as Pt, PSS, and PH1000, respectively, in all figures.

The morphology of PEDOT:PSS films spun on plastic polyetherimide substrates was studied using atomic force microscopy (AFM). Fig. 1 shows the phase image of doped (top) and undoped PEDOT:PSS (bottom) films. The phase image of PEDOT:PSS doped with approximately 4 wt. % DMSO shows a fibrous morphology with connecting PEDOT chains (bright regions) in a matrix of PSS (dark). It is well known that the addition of solvents like DMSO and ethylene glycol (EG) induces phase segregation at the nanometer level in PEDOT:PSS films. Due to a thermodynamically driven rearrangement, the PSS phase segregates into insulating domains (dark regions in phase image), while highly conducting PEDOT grains merge together to form a three dimensional conducting network (bright fibers in phase image). The presence of conducting PEDOT chains through which charge carriers can move freely leads to the high conductivity seen in doped PEDOT:PSS films. On the other hand undoped PEDOT:PSS films show a granular morphology with the presence of isolated PEDOT domains in a matrix of insulating PSS phase. This leads to an increase in sheet resistance of undoped PEDOT:PSS films as seen from Table I.

TABLE I. Conductivities of different PEDOT:PSS grades, characterized using a four probe measurement system. Clevios PH500 and PH1000 were doped with 4% DMSO. All films were spun at 1500 rpm for 30 s.

<table>
<thead>
<tr>
<th>PEDOT:PSS grade</th>
<th>PSS</th>
<th>PH500</th>
<th>PH1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>95 ± 5</td>
<td>45 ± 5</td>
<td>65 ± 5</td>
</tr>
<tr>
<td>Sheet resistance (Ω/sq)</td>
<td>~1.37 × 10⁴</td>
<td>~4.3 × 10²</td>
<td>~1.7 × 10²</td>
</tr>
<tr>
<td>Conductivity (S/cm)</td>
<td>~0.768</td>
<td>~520</td>
<td>~915</td>
</tr>
</tbody>
</table>

FIG. 1. AFM phase image of a 0.5 × 0.5 μm² area with top half showing morphology of doped PEDOT:PSS and bottom half of undoped PEDOT:PSS film.

FIG. 2. (a) Polarization (P) vs. electric field (E) hysteresis loop measurements at a frequency of 10 Hz. Inset shows a magnified image of coercive fields for devices with different bottom electrodes, (b) switching characteristics for ferroelectric capacitors at 120 MV/m, with peak of dP/d(log t) vs. log t representing respective switching times. Inset shows a switching event with sharp increase in polarization at corresponding switching times.
unfavorable increase in coercive fields \((+E_f/-E_e)\) is from \([-+58/-53]\) MV/m using metal electrodes to \([+70/-65]\) MV/m] using PEDOT:PSS bottom electrodes. We believe this can be attributed to the poor conductivity of the undoped PEDOT:PSS which leads to a large voltage drop across the unpatterned bottom electrode. The undoped and poorly conducting PEDOT:PSS film acts as a large resistor connected in series with the ferroelectric capacitor. This is also indicated by the AFM image of un-doped PEDOT:PSS films shown above, which shows the presence of excess insulating PSS leading to resistor like behavior from these unpatterned films. The intrinsic coercive field of the ferroelectric film itself does not change. Instead, a higher voltage is needed to reach the required coercive field to switch the dipoles in the ferroelectric copolymer film. To further confirm this effect, we fabricated a device with bottom Pt electrodes and a thin interfacial layer of undoped PEDOT:PSS (\(\sim 20\) nm), referred to as Pt-PSS in all figures. The devices with an interfacial layer of undoped, poorly conducting PEDOT:PSS exhibit coercive fields of \(+58\) MV/m and \(-50\) MV/m, similar to devices with metal electrodes. This result confirms the fact that the apparent high coercive voltage measured in devices using undoped PEDOT:PSS as a standard electrode is not intrinsic. Instead, it is related to an extrinsic voltage drop due to the large resistance of the electrode. This result may also explain some of the high coercive voltages reported for P(VDF-TrFE) devices with polymer electrodes.\(^{12}\)

In parallel, we have also fabricated devices with highly conducting, doped PEDOT:PSS electrodes. Devices with highly conducting, doped PEDOT:PSS electrodes displayed coercive fields similar to devices with metal electrodes \((+60\) MV/m and \(-54\) MV/m). The presence of highly conducting network of PEDOT chains as seen from the AFM characterization shown above ensures minimal voltage drop across the unpatterned bottom electrode. This substantial improvement in coercive fields compared to the low-conductivity PEDOT:PSS suggests the possibility of using doped PEDOT:PSS for fabrication of low-voltage, transparent, and flexible ferroelectric memory.

Switching characteristics of our P(VDF-TrFE) copolymer films are shown in Fig. 2(b), which can be obtained by a time domain measurement of the charge density or polarization (P) response. As seen from the inset of Fig. 2(b), polarization plotted against logarithmic time \((\log t)\) exhibits a rapidly increasing curve during dipole switching. Switching times \((\tau_s)\) are estimated from the time of the maximum of \text{dP/d(log)t} vs. \text{log (t)} plot.\(^{13}\) At applied fields of \(120\) MV/m, devices with Pt electrodes exhibit switching times of \(10.7\) ms while devices with bottom PEDOT:PSS electrodes have increased switching times of \(13.35\) ms. This can be explained based on the dependence of switching time, \(\tau_s\), on applied electric field,\(^{13}\) given by Eq. (1)

\[
\tau_s = \tau_{s\infty}e^{E_a/E},
\]

where \(\tau_{s\infty}\) is the limited switching time, \(E_a\) is the activation field, and \(E\) is applied electric field. Thus, the switching time increases for lower applied fields in ferroelectric capacitors. For undoped (poorly conducting) PEDOT:PSS electrodes, the voltage drop across the bottom electrode leads to lower applied fields across the ferroelectric film, leading to increased switching times. However, devices with an interfacial layer of undoped PEDOT:PSS and doped PEDOT:PSS electrodes have lower switching times of \(\sim 10.7\) ms, identical to devices with metal electrodes.

Fig. 3(a) shows the dielectric dispersion and the loss factor (\(\tan \delta\)) of P(VDF-TrFE) ferroelectric capacitors. A decay of the dielectric constant is seen, consistent with the dielectric response of ferroelectric thin films.\(^{14-17}\) Our P(VDF-TrFE) copolymer films exhibit a dielectric constant of \(\sim 11.5\) at 100 Hz, comparable to other reports in the literature.\(^{3}\) Devices with Pt bottom electrodes have excellent dielectric performance even at a high frequency of 1 MHz, with a negligible drop in permittivity and low losses. Devices with poorly conducting PEDOT:PSS electrodes show a step-like decrease of the permittivity up to a frequency of \(\sim 7\) kHz. This reduction is mainly caused due to loss of interfacial polarization at the dielectric-electrode interface, indicated by a peak in the imaginary part of the permittivity, \(\varepsilon''\) (Fig. 3(b)) resembling a Debye-like dipolar relaxation.
Further drop in the permittivity beyond 7 kHz can be attributed to the series resistance from the undoped PEDOT:PSS electrodes, absent in the devices with doped PEDOT:PSS bottom electrode. The dielectric response of ferroelectric capacitors can be represented with an equivalent circuit consisting of a resistor in series with a parallel RC circuit.\textsuperscript{14,16} The capacitor shows an RC time constant behavior determined by $\tau = R_s C_f$, where $R_s$ is the series resistance from the electrode and $C_f$ is the film capacitance. Higher series resistance from the electrodes indicates that the fall-off would occur at lower frequencies, which in our case is attributed to the poor conductivity of undoped PEDOT:PSS. This limits the use of poorly conducting PEDOT:PSS electrodes to low frequency applications.

Fig. 3(a) also shows the dielectric losses (tan $\delta$) calculated from the ratio of the imaginary and real part of the dielectric constant (Eq. (2)). For undoped, poorly conducting PEDOT:PSS electrodes, the increase in losses up to $\sim$7 kHz can be attributed to an increase in the imaginary part of the permittivity, $\varepsilon''$, that is the Debye loss peak. Beyond this, the series resistance effect that dominates is manifested by a sharp increase in losses (Fig. 3(a)) and the real part of conductivity ($\sigma'$) (Fig. 2(b))\textsuperscript{14,15}
\begin{equation}
\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\sigma'}{\varepsilon_0 \omega C_f}.
\end{equation}

More importantly, here we demonstrate that upon using highly conducting doped PEDOT:PSS electrodes, it is possible to get devices with excellent dielectric response and low losses up to 1 MHz, frequencies applicable to many basic logic and memory operations.

Fig. 4 shows the small signal capacitance measured by superimposing a small AC electric field (50 mV, 10 KHz) over DC field sweep from $-15$ to $+15$ V. The characteristic “butterfly” shape of the C-V curve indicates ferroelectric switching phenomenon with the two peaks corresponding to dipole reversal. The 120 nm thick P(VDF-TrFE) films on metal electrodes display a peak capacitance of $\sim$65 nF/cm$^2$. This is identical to devices with undoped interfacial PEDOT:PSS layer and doped highly conducting PEDOT:PSS electrodes. In contrast, there is an approximate 40% drop in capacitance density to $\sim$37 nF/cm$^2$ upon using undoped PEDOT:PSS electrodes. The drop in capacitance confirms the series resistance effect, as discussed using dielectric spectroscopy in Fig. 3.

The fatigue behavior of ferroelectric capacitors with metal and polymer electrodes is compared in Fig. 5. A bipolar triangular waveform with an amplitude of 10 V and 10 ms pulse width was applied during fatigue, and the devices were characterized periodically with a positive-up-negative-down (PUND) measurement at 15 V at the same frequency. Devices with metal electrodes display significant fatigue with only 20% retention after $10^6$ cycles. Fatigue in P(VDF-TrFE) is very sensitive to the applied field and frequency of stress cycles, with increased fatigue at high field and low frequencies.\textsuperscript{20,21} Fatigue performance of our devices with metal electrodes is consistent with other reports in the literature at similar frequencies.\textsuperscript{20,22} Devices with bottom polymer electrodes show a slight improvement with 31% and 44% retention for highly and poorly conducting PEDOT:PSS electrodes, respectively. There have been various studies published on the effect of applied voltage profile, frequency, crystallinity, and operating temperature on polarization fatigue, but most of these studies were done using metal electrodes on silicon substrates.\textsuperscript{21,23,24} In contrast, there have been very limited reports on fatigue using polymer electrodes.\textsuperscript{12} It has been proposed that fatigue in P(VDF-TrFE) film is related to the injection of charges from electrodes which are subsequently trapped at crystallite boundaries and defects, inhibiting ferroelectric switching and leading to higher fatigue rates.\textsuperscript{5,21} Our fatigue data show that after $10^5$ cycles, devices with bottom Pt electrodes retain about 42%, doped PEDOT:PSS devices retain 60% while undoped PEDOT:PSS devices retain as much as 68% of the initial polarization. We believe that the use of poorly conducting polymer electrodes reduces charge injection into the P(VDF-TrFE), resulting in less trapped charges, therefore lower fatigue rates. Thus it is evident that while the devices made from the undoped, poorly conducting...
PEDOT:PSS exhibit inferior performance, their fatigue characteristics are greatly improved. Based on the data, using doped PEDOT:PSS with high conductivity appears to be a promising material for use as local and global interconnect in flexible, transparent electronics applications. It exhibits metal-like behavior and with improved fatigue retention properties.

In summary, we have demonstrated that by using highly conducting doped polymer electrodes (PEDOT:PSS with 4% DMSO), we can fabricate ferroelectric devices with good polarization, low coercive fields, low dielectric losses, comparable to devices with metal electrodes. Furthermore we have shown the added advantage of using polymer electrodes, in the improved fatigue performance of ferroelectric capacitors. This is a major advancement in the performance and opens the possibility of fabricating all-polymer ferroelectric memory devices for plastic electronics.

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