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Solution-processed nanocomposite dielectrics for low voltage operated OFETs

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Abstract
A novel, solution processed high-k nanocomposite/low-k polymer bilayer gate dielectric that enables the fabrication of organic field-effect transistors (OFETs) that operate effectively at 1 V in high yields is reported. Barium strontium titanate (BST) and barium zirconate (BZ) nanoparticles are dispersed in a poly (vinylidene fluoride-co-hexafluoropropylene) P(VDF-HFP) polymer matrix to form a high-k nanocomposite layer. This is capped with a thin layer (ca 30 nm) of cross-linked poly(vinyl phenol) (PVP) to improve the surface roughness and dielectric–semiconductor interface and reduces the leakage current by at least one order of magnitude. OFETs were fabricated using solution-processed semiconductors, poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]thiophene and a blend of 6,13-bis (triisopropylsilylethynyl) pentacene and poly (α-methylstyrene), in high yield (>90%) with negligible hysteresis and low leakage current density (10^{-6} A cm^{-2} at ±1).

1. Introduction
The rapid development of organic semiconductor materials that can be processed from solution opens up the possibility of printing organic field-effect transistors (OFETs) onto a wide range of substrates to enable the development of low-cost, large area electronics [1,2]. However, typical solution-processed OFETs operate at voltages that are too high for use in portable electronic devices or as aqueous sensors (V > 5 V) [3,4]. For these applications, transistors working in the range of 1.5–1 V are highly desirable. Lowering the operational voltage of OFETs can be achieved by reducing the threshold voltage and the subthreshold swing. These device parameters are largely controlled by the gate dielectric and the density of charge traps at the dielectric–semiconductor interface. Therefore, to achieve operational voltages approaching 1 V, high-capacitance, solution-processable gate insulators that form trap-free interfaces are essential.

In a field-effect transistor, the gate voltage (V_G) required to switch the transistor “on” scales directly with insulator thickness, d, and inversely with insulator dielectric constant, k: V_G ≈ d/k. Usually, organic dielectrics have relatively low dielectric constants (k ≈ 2–4) [5,6] and hence extremely thin layers (d < 20 nm) are required to obtain low-voltage transistor operation. Recently, organic transistors that operate at 4 V have been demonstrated using 10 nm cross-linked polymer and polymers blends [7,8], or self-assembled mono- [9] and multi-layer [10] (SAM) (d ~ 2.8 nm) insulators. Alternatively, 1 V OFETs using anodized TiO_2 (k = 20–41, d = 7.5 nm) have been reported [11,12]. Organic transistors operating below 4 V have been demonstrated using solution-processed high-k dielectrics

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such as barium titanate (BT) nanocomposites \((k \sim 12)\) [13] or relaxor ferroelectric polymers, i.e. poly (vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) \((P(VDF–TrFE–CFE))\) terpolymer \((k \sim 60)\) [14]. Achieving OFET operation down to 1 V requires both minimizing \(d\) and maximizing \(k\), and this leads to practical problems. For example, thin dielectric layers may be too fragile for flexible operation leading to an increase in the gate leakage current, whereas thicker films of high-\(k\) insulators introduce undesirable effects at the organic semiconductor–insulator interface. This can lead to increased charge trapping that causes a rise of threshold voltage \((V_t)\) and inverse subthreshold slope \((SS)\), as well as, lowering the field effect mobility of charge carriers in OFETs [15,16]. Therefore, the fabrication of OFETs working at or below 1 V using both solution-processable semiconductors and high-\(k\) dielectrics is still very challenging.

Herein, we show that OFETs operating below 1 V can be successfully fabricated in high yield with low device hysteresis and gate leakage using a solution-deposited high-\(k\) nanocomposite/low-\(k\) polymer bilayer gate dielectric. The first layer is a high-\(k\) organic insulating polymer filled with very high-\(k\) ceramic nanoparticles that is partially capped by a second low-\(k\) polymer dielectric layer. One of the key challenges in the formation of high quality, high-\(k\) nanocomposite layers is to control the homogeneity of the nanoparticle dispersion and the stability of the nanocomposite suspension. The high surface energy and surface-to-volume ratio of nanoparticles usually results in agglomeration and phase separation from the polymer matrix, particularly at high filler loading, leading to an inhomogeneous mixture with poor processability, increased porosity and defect density [17]. Percolative pathways can be created through the aggregated fillers that leads to increased leakage current density, reduced dielectric breakdown strength and decreased dielectric constant [18]. Surface modification of the nanoparticles with a suitable coupling agent is one of the most widely used methods to prevent nanoparticle agglomeration. Such treatments promote interfacial interactions between the nanoparticles and the polymer matrix and thus improve the uniformity of the nanoparticle dispersion [19]. In this work, a stable, homogenous nanocomposite dispersion was prepared by incorporating high-\(k\), perovskite-phase metal oxide nanoparticles of barium strontium titanate \((BST, k \sim 16)\) [20] and barium zirconate \((BZ, k \sim 32)\) [21] into a poly (vinylidene fluoride-co-hexafluoropropylene) \((P(VDF-HFP))\) polymer matrix \((k \sim 11)\). By carefully identifying the best combination of fluorinated copolymer, organic solvents and nanoparticle-to-polymer volume ratio, a reproducible, uniform nanocomposite suspension was made without the need for further nanoparticle surface modification.

2. Experimental

\(P(VDF-HFP)\) pellets \((50\text{ mg ml}^{-1})\) were dissolved in N,N-dimethylformamide \((\text{DMF})\) and stirred for a minimum of 6 h. Various volume ratios \((7:1–1.25:1)\) of BST or BZ nanoparticles were dispersed in \(P(VDF-HFP)\) solution, followed by a 2-h ultrasonication \((80\text{ W})\) and thereafter stirring for minimum 12 h to further promote uniform dispersion of nanoparticles. The nanocomposite suspension was then centrifuged at 6000 rpm for 5 min to separate any larger particles and agglomerates to obtain a homogeneous suspension. The resultant nanocomposite suspension was stable and no apparent precipitation was observed for several weeks at room temperature.

To evaluate the transistor performance, bottom-gate, bottom-contact OFETs were fabricated using either solution-processed poly(3,6-di(2-thien-5-yl)-2,5-di(2-octyldodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)thieno[3,2-b]-thiophene \((\text{PDPPTT})\) [22] or a blend of 6,13-bis (trisopropylsilyl-ethyl)-pentacene \((\text{TIPS-Pentacene})\) and poly(\(\alpha\)-methylstyrene) \((\text{PMS})\) [23] as the active layer. OFETs were fabricated on Corning\textsuperscript{®} glass substrates on which a 100 nm aluminum \((\text{Al})\) layer was thermally evaporated to serve as the gate electrode. The Al surface was briefly treated with UV–Ozone prior to spin-coating the nanocomposite dielectric layer. The nanocomposite dielectric film was formed by spin-coating \(P(VDF-HFP)\)-based nanocomposite suspension at 3000 rpm for 2 min and annealing at 90 °C for 90 min. A capping layer of poly(vinyl phenol) \((\text{PVP})\) \((20\text{ mg ml}^{-1})\) in propylene glycol monomethyl ether acetate \((\text{PGMEA})\) with added poly (melamine-co-formaldehyde) \((\text{PMF})\) \((10\text{ mg ml}^{-1})\) cross-linking agent was spin-coated on top of the nanocomposite layer at 5000 rpm for 2 min, followed by cross-linking at 130 °C for 90 min under nitrogen. Gold \((\text{Au})\) source and drain electrodes \((50\text{ nm})\) were deposited through a shadow mask by thermal evaporation. Au contacts are then modified by submersing samples in a 10 mM 2,3,4,5,6-pentafluorothiophenol \((\text{PFBT})\) solution followed by repeated washing with 2-propanol \((\text{IPA})\). For devices using the semiconductor blend, a 7:3 by weight \((10\text{ mg ml}^{-1})\) of \(\text{TIPS-Penta-cene:PxMS}\) solution was spin-coated at 500 rpm for 2 min, followed by heating the sample at 60 °C for 20 min under \(\text{N}_2\). \(\text{PDPPTT}\) was deposited by spin-coating a solution \((10\text{ mg ml}^{-1})\) at 1000 rpm for 1 min and subsequently heating the sample at 110 °C for 30 min under \(\text{N}_2\).

Device characterization was performed in ambient air using an Agilent E5270B measurement mainframe with Karl Suss PH100 micromanipulator probes. AFM images were recorded on a Bruker Multimode 8 in Peak Force tapping mode at a resolution of 512 × 512 pixels. Cantilevers had a spring constant of approximately 0.350 N m\(^{-1}\), with a resonant frequency of approximately 50–80 kHz. A modulation frequency of 2 kHz was used. The TEM micrograph was obtained using a JEM2000FX2 \((\text{JEOL})\) instrument operating at an acceleration voltage of 120 kHz. The TEM specimen was prepared on an ultramicrotome EM UC6 \((\text{Leica})\) with a slice thickness of 50 nm.

3. Results and discussions

The dielectric properties of the prepared nanocomposite films were evaluated by the fabrication of parallel-plate capacitors. As shown in Fig. 1(a), solution processed \(\text{BST}\)-\(P(VDF-HFP)\) dielectric layers showed leakage currents at \(\pm 1\text{ V}\) up to \(10^{-7}\text{ A cm}^{-2}\). Similar leakage current behavior was observed in analogous BZ-\(P(VDF-HFP)\) films (Fig. 2(a)). To improve the electrical performance, a thin layer of PVP
was applied to the surface of the nanocomposite films. Unlike reported previously [14,24], the thickness of the PVP capping layer was carefully tailored to only partially cover the topographic features of the rough nanocomposite surface (Figs. 1(b–c) and 2(b–c)), as this ensured that no significant loss of capacitance was observed. Deposition of a thin PVP layer ($d = 20–30$ nm) decreased the leakage current density by at least one order of magnitude to $10^{-9}$ A/cm$^2$ at ±1 V, Figs. 1(a) and 2(a), and lowered the RMS surface roughness of the nanocomposite film from 28 nm to 20 nm and from 39 nm to 29 nm for PVP-capped BST- and BZ-nanocomposite films respectively. The capacitance ($C$, pF) of the nanocomposite bilayers was measured at a 500 Hz–1 MHz frequency range. At 1 kHz, the areal capacitance ($C_i$) decreased from $93.7 \pm 0.2$ nF cm$^{-2}$ ($d = 148 \pm 0.3$ and $k = 15.7 \pm 0.4$) for the uncapped BST-nanocomposite layer to $64.4 \pm 0.2$ nF cm$^{-2}$ ($d = 178 \pm 0.2$ and $k = 13.2 \pm 0.2$) for the bilayer dielectric. Thicker films of PVP ($d > 100$ nm) led to a significantly reduced $C_i$ of $8.70 \pm 0.06$ nF cm$^{-2}$. The contact angle of water was reduced from $89^\circ$ to $77^\circ$, additionally confirming the presence of the PVP. Similarly, a reduction in $C_i$ from $72.3 \pm 0.8$ nF cm$^{-2}$ ($d = 269.0 \pm 0.6$ and $k = 21.9 \pm 0.4$) to $27.5 \pm 0.3$ nF cm$^{-2}$ ($d = 293.0 \pm 0.1$ and $k = 8.9 \pm 0.4$) was measured when BZ-nanocomposite dielectric layer was capped with PVP.

A sectional TEM image of the completed TIPS-Pentacene and P$\alpha$MS OFET with PVP-capped BST-P(VDF-HFP) nanocomposite layer is shown in Fig. 1(d), clearly showing the high surface roughness of the nanocomposite film. For pristine high-$k$ nanocomposite layers, only poorly operating OFETs could be fabricated due to the large roughness

![Fig. 1. (a) Leakage current density of BST-P(VDF-HFP) nanocomposite dielectric films. Tapping mode AFM images of adhesion profile of (b) uncapped and (c) PVP-capped BST-P(VDF-HFP). (d) Cross-sectional TEM image of a TIPS-Pentacene/P$\alpha$MS OFET with PVP-capped BST-P(VDF-HFP) nanocomposite layer.](image-url)
and difficulties with deposition of the semiconductors from solution on the surface of the fluorinated polymer. Bilayer dielectric films of nanocomposites with thick PVP films ($d > 100$ nm) produced OFETs that operated well above 5 V with a leakage current density $<10^{-11}$ A cm$^{-2}$. Bilayer dielectrics with PVP layers of 20–30 nm resulted in high yields (>90%) of working OFETs that operate at 1 V.

Transfer and output characteristics of the BZ-P(VDF-HFP) OFETs using TIPS-Pentacene/PzMS are shown in Fig. 2(d–e). It was found that those devices could not be operated below 1 V due to a high threshold voltage ($V_T = -0.85$ V). This is believed to be due to larger thickness and surface roughness and thus smaller $C_i$ of BZ-P(VDF-HFP) nanocomposite layers. However, working OFETs operating at under 1.5 V with very small hysteresis, a leakage current density $<10^{-9}$ A cm$^{-2}$ at ±1.5 V and a mobility at 1.5 V of 0.08 cm$^2$ V$^{-1}$ s$^{-1}$ were achieved. The full device characteristics for BZ-P(VDF-HFP) as the dielectric layer are shown in Table 1. Subsequently, BST-P(VDF-HFP) OFETs using PDPPTT and TIPS-Pentacene/PzMS were fabricated (Fig. 3(a–b) and (c–d), respectively). In both cases the devices turned on below 1 V ($V_T \sim -0.5$ V). The transfer and output characteristics were virtually hysteresis-free and the leakage currents were at least one order of magnitude below “on” currents; clear “off” and “on” operating states could be distinguished. The average field-effect mobility for the 1 V OFETs was calculated to be 0.14 cm$^2$ V$^{-1}$ s$^{-1}$ for the PDPPTT devices and 0.06 cm$^2$ V$^{-1}$ s$^{-1}$ for those with TIPS-Pentacene/PzMS as the active layer. Transistors with the semiconductor blend as the active layer
showed a lower subthreshold slope ($S = 169 \text{ mV dec}^{-1}$) and one order of magnitude lower leakage current density than those fabricated with PDPPTT (c.f. Table 1). It appears that the vertical phase separation occurring within the semiconductor blend [25], in which the TIPS-Pentacene layer is sandwiched between two layers of P$_{a}$MS, contributes to a more robust and trap-free interface at the gate dielectric.

4. Conclusion

In summary, solution-processed dielectric layers suitable for 1 V operation of OFETs with polymeric and small molecule organic semiconductors are reported. The dielectric layer consists of a bilayer film composed of a high-$k$ nanocomposite film that is partially capped by a low-$k$ polymer. The OFET devices are prepared in high yield (>90%), operate with minimal hysteresis, display very low subthreshold slope (<200 mV dec$^{-1}$) and possess mobilities reaching 0.1 cm$^2$ V$^{-1}$ s$^{-1}$ at 1 V. These materials are promising candidates for fabrication of OFETs suitable for use in aqueous based biosensors and low power electronics.

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