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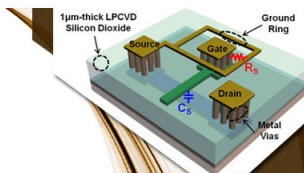
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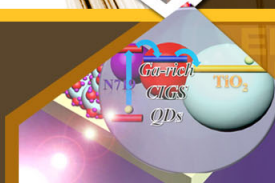
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Solution-processible high-permittivity nanocomposite gate insulators for organic field-effect transistors

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We report on solution-processible high permittivity nanocomposite gate insulators based on BaTiO₃ nanoparticles, surface-modified with a phosphonic acid, in poly(4-vinylphenol) for organic field-effect transistors. The use of surface-modified BaTiO₃ nanoparticles affords high quality nanocomposite thin films at large nanoparticle volume fractions (up to 37 vol %) with a large capacitance density and a low leakage current (10⁻⁸ A/cm²). The fabricated pentacene field-effect transistors using these nanocomposites show a large on/off current ratio ($I_{\text{on/off}}$ 10⁴–10⁶) due to the high capacitance density and small leakage current of the gate insulator. © 2008 American Institute of Physics. [DOI: 10.1063/1.2949320]

Research on organic field-effect transistors (OFETs) has advanced rapidly in recent years, as low-voltage, flexible, inexpensive, large-area transistors are proving to be a promising technology.^{1–3} While most research efforts have focused on the development of new semiconductors with high mobility, only recently have gate insulators and their interfaces with organic semiconductors been investigated.^{3–11} One potentially viable approach to obtain useful drain currents (I_D) from OFET devices is to increase the capacitance density of the gate insulator. Recently, some inorganic high-permittivity (κ , relative permittivity) dielectrics have been developed to provide increased capacitance in OFETs.^{10,12} However, their limited processibility and poor interfacial characteristics with organic semiconductors remain problematic. In contrast, polymer dielectrics have excellent processibility and compatibility with organic semiconductors, yet their capacitance is limited by their low permittivity.^{3,13,14}

Combining high- κ dielectric nanoparticles with polymers has recently been the focus of several studies seeking to obtain materials that are solution processible and exhibit high capacitance suitable for gate insulators in OFET.^{4,6–8,11} However, OFETs using these nanocomposite gate insulators, typically with less than 5% particles by volume, small on/off current ratios ($I_{\text{on/off}}$ 10³–10⁴) due mainly to large leakage current.^{1,4,8,11} To obtain higher capacitance, larger volume fractions (>30%) of nanoparticles are needed but this usually leads to poor film quality due to nanoparticle aggregation. As a result, large leakage currents and low breakdown strength are obtained from these films. To avoid these problems, especially at high volume fractions of nanoparticles, better control over the particle-particle interaction and particle-polymer interfaces is required. Phosphonic acids have recently been found to form a robust surface layer on barium titanate (BT) nanoparticles with high surface coverage, which decreases nanoparticle aggregation and improves the quality of the resultant nanocomposite films.¹⁵

In this paper, we report on solution-processible, high-quality nanocomposite thin films utilizing high volume fractions (up to 37 vol %) of phosphonic acid-coated BT nanoparticles dispersed in a crosslinkable polymer, poly(4-vinylphenol). The use of these thin films as gate insulators in pentacene OFETs resulted in a large on/off current ratio ($I_{\text{on/off}}$ ~10⁶) due to the reduced leakage current (~10⁻⁸ A/cm²). Additionally, the saturation mobility of the pentacene layer was found to be greatly influenced by the increased surface roughness of the underlying nanocomposite films. By combining high volume fraction nanocomposites with a thin planarization layer of a pure polymer, a saturation mobility of 0.17 cm²/V s and an output current of ~10⁻⁵ A were obtained.

BT nanoparticles (30–50 nm, κ ~ 150, Aldrich) were modified with {2-[2-(2-methoxyethoxy)ethoxy]ethyl}-phosphonic acid (PEGPA) (see Fig. 1) as described previously,¹⁵ then dispersed in 1-butanol with poly(4-vinylphenol) (PVP) (M_w ~ 20 000, Aldrich), hexamethoxymethyl-

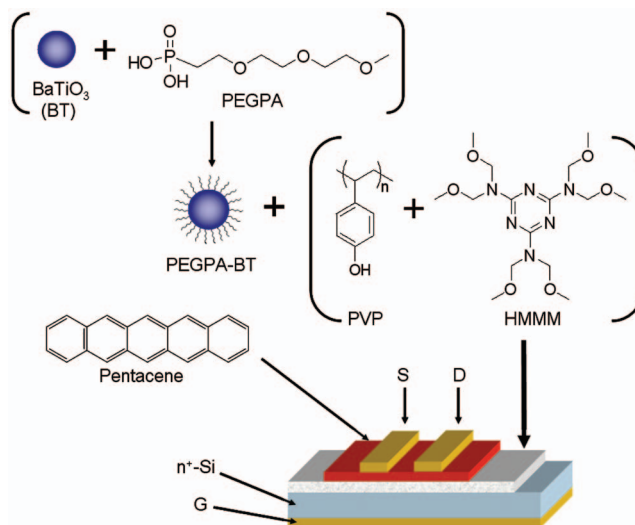


FIG. 1. (Color) Schematic of PEGPA-BT:PVP nanocomposite preparation and the structure of OFET devices fabricated.

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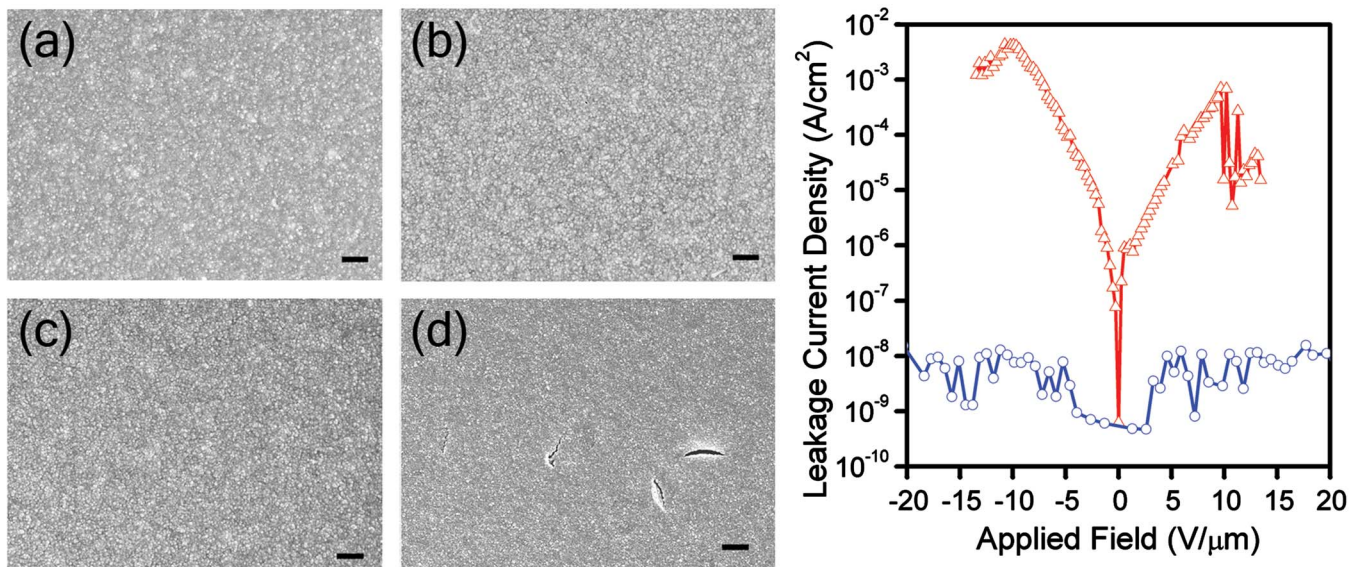


FIG. 2. (Color online) Left: SEM images of PEGPA-BT:PVP nanocomposite thin films with nanoparticle volume fractions of 16 vol % (a), 28 vol % (b), and 37 vol % (c), respectively. 37 vol % film of unmodified BT (d) is shown for comparison. Scale bars represent 1 μm . Right: comparison of the leakage current densities of nanocomposite thin films containing 37 vol % of surface-modified BT (circle, $t=305$ nm, 37 nF/cm²) and unmodified BT (triangle, $t=744$ nm, 14 nF/cm²).

melamine (HMMM) (Cyamel 300, Mitsui Cyanamide) as a crosslinker, and a catalytic amount of *p*-toluenesulfonic acid (TsOH) (Aldrich) (PVP:HMMM:TsOH=15:5:1 by weight). The ratio of PEGPA-modified BT (PEGPA-BT) to PVP was varied from 16% to 37% by volume. The nanocomposite dispersion homogenized by ball milling was spin coated on cold air plasma treated ⁵ *n*-doped Si wafers having a Ti/Au (10/100 nm) backside contact. The films were soft baked at 100 °C for 1 min and thermally cured under vacuum at 160 °C for 72 h to ensure full crosslinking of PVP. Control samples were prepared in the same way using unmodified BT nanoparticles. Bottom gate and top contact *p*-type OFETs of various channel widths and lengths were fabricated on top of the nanocomposite thin films by physical vapor deposition of 50 nm thick pentacene films at room temperature, followed by deposition of Au/Al (40/100 nm) electrode, Fig. 1. Capacitors using the nanocomposite films were also fabricated for dielectric characterization. Films were characterized using a Dektak contact profilometer, a LEO 1530 scanning electron microscope (SEM), and a Dimension 3100 atomic force microscopy (AFM). The capacitors and OFETs were characterized in a nitrogen-filled glove box using an Agilent 4284A LCR meter and an Agilent E5272A source/monitor unit, respectively.

Figure 2 shows SEM images of the nanocomposites prepared on Si substrates revealing the uniformity of the thin films over large areas for the fabrication of multiple OEFT devices. The nanocomposite gate insulators prepared using

surface-modified BT showed significantly reduced leakage current density than those using unmodified BT as shown in Fig. 2. The lower leakage current can be attributed to reduction of direct particle-particle contacts and improved dispersion of the BT nanoparticles in the PVP matrix. The surface passivation of ionizable hydroxyl groups by the phosphonic acid is also thought to reduce the leakage current by eliminating possible charge conduction pathways in the film.¹⁵

The properties of the nanocomposites with varying amounts of BT are summarized in Table I. As the volume fractions of BT nanoparticles increased so did the permittivity (from 4 with no BT to 14 with 37 vol % BT). By changing the viscosity of the nanocomposite dispersion and the spin speed to control thickness, the capacitance density could be increased to ~ 50 nF/cm². It should be noted that the rms roughness of the nanocomposite surface increased and the carrier mobility decreased with increasing the volume fraction of BT (Table I). The field-effect carrier mobility of the semiconductor is closely related to its microstructure and morphology, which in turn can be influenced by the interface between the semiconductor and the underlying layer.^{1,2,9,16} The surface roughness of the nanocomposites at high nanoparticle-filling conditions was quite large compared to that of pure PVP films. Consequently, the morphology of pentacene semiconductor films deposited on top of the nanocomposite gate showed a small grain size and a morphology that mimicked the underlying nanocomposite, as shown in Fig. 3.

Application of a thin polymer layer has been shown to planarize the rough surface of nanocomposite layers and can

TABLE I. Properties of PEGPA-BT:PVP nanocomposite thin films. C : capacitance density, J_L : average leakage current density measured over ± 20 V/ μm , μ : charge mobility. RMS roughness is from a 5×5 μm^2 area (for pure PVP, rms=0.26 nm).

vol % BaTiO ₃	Thickness (nm)	κ (1 kHz)	C (nF/cm ²)	J_L (A/cm ²)	rms roughness (nm)	μ (cm ² /V s)
16	250	6.0	22	$\sim 1 \times 10^{-8}$	6.16	0.34
28	386	9.6	22	$\sim 1 \times 10^{-8}$	7.80	0.11
37	406	14.0	31	$\sim 1 \times 10^{-8}$	8.81	0.04

TABLE II. Summary of the OFET device characteristics described in Fig. 4. rms roughness from a 5×5 μm^2 scan area.

	t (nm)	C (κ) (nF/cm ²)	rms roughness (nm)	μ (cm ² /V s)	V_T (V)	S (V/decade)	$I_{\text{on/off}}$
NC only	406	31 (14)	8.81	0.04	-1.96	0.67	6×10^4
NC/PVP	251	42 (12)	3.76	0.17	-1.1	0.3	2.3×10^5

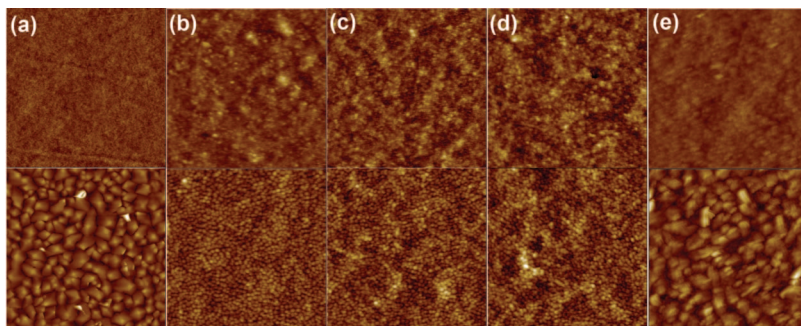


FIG. 3. (Color) AFM height images of gate insulator surfaces (top row) and pentacene layer deposited on each surface (bottom row). (a) Pure PVP. [(b)–(d)] PEGPA-BT:PVP nanocomposites with 16, 28, and 37 vol % BT, respectively. (e) 37 vol % PEGPA-BT:PVP nanocomposite with a planarization layer of pure PVP. Image size = $5 \times 5 \mu\text{m}^2$, height = 100 nm, except for pure PVP (height = 5 nm).

improve the interfacial properties, including reducing the trap density and changing the relative surface energies between the layers.^{6,9,11} By spin coating a 5% by weight solution of PVP in 1-butanol on top of the nanocomposite layer, the surface roughness was significantly reduced and the morphology of pentacene was dramatically changed, resulting in large grains, as shown in Fig. 3, which are crucial for high carrier mobility.¹⁶ Though there was a slight reduction in the effective permittivity of the insulator due to this additional layer, the final permittivity ($\kappa=12$) was still three times larger than that of pure crosslinked PVP ($\kappa=4$). Additionally, the leakage current was further reduced by a factor of $\sim 2\text{--}5$ after the application of the planarization layer.

In order to quantitatively compare the effect of the planarization layer, devices with the same ratio of channel width and length were analyzed and their characteristics are summarized in Fig. 4 and Table II. The dependence of the saturation mobility of an organic semiconductor on the permittivity of the gate insulator has recently been studied.^{6,13} In our high- κ nanocomposites, the mobility was influenced to a greater extent by the morphology of the semiconductor than the permittivity of the gate insulator. The combined effect of the high- κ insulator using high volume fractions, low leakage current by surface modification, and the increased saturation mobility up to $0.17 \text{ cm}^2/\text{V s}$ by using a thin planarization layer yielded OFET devices with a low threshold voltage (-1.1 V), a small subthreshold swing (0.3 V/decade), and a large on/off current ratio (2.3×10^5).¹⁷ In order to further reduce the leakage current, OFET devices

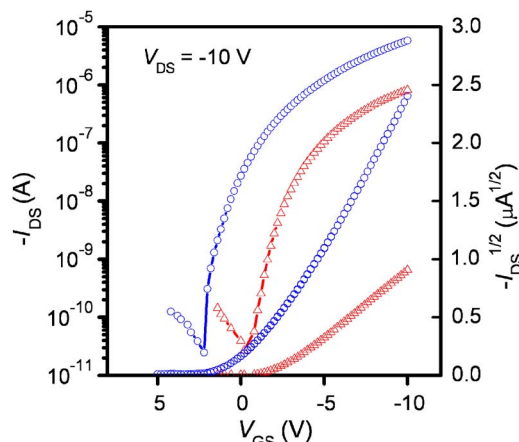


FIG. 4. (Color online) OFET transfer characteristics obtained from the devices ($W/L=20, 500 \mu\text{m}/25 \mu\text{m}$ for NC only and $2000/1000 \mu\text{m}$ for NC/PVP) fabricated on 37 vol % PEGPA-BT in PVP nanocomposite gate insulators without a planarization layer (triangle) and with a planarization layer (circle).

with patterned pentacene to reduce the metal-semiconductor contact area were fabricated and a larger on/off ratio (1.2×10^6) was observed using our nanocomposite gate insulators.

In conclusion, we have shown that the use of surface-modified BT nanoparticles allows for solution processible, high quality, high- κ , and low leakage current nanocomposite thin films suitable for gate insulators in OFETs. Surface modification of the nanoparticles result in improved on/off current ratio due to the effective reduction of leakage current. The problem of the high surface roughness of the nanocomposite layer at high filler fraction can be addressed by using a thin planarizing layer. It can be expected that a further increase in the capacitance density is possible by optimization of surface-modified nanoparticle/polymer composite approach by increasing the filler volume fractions and/or using a higher permittivity polymer host and nanoparticles.

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¹⁷Due to the residual hydroxyl groups present in PVP, it may not be applicable to n -type semiconductors.