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COMMUNICATION

Formulation of Novel Screen-Printable Dielectric Ink for Fully-Printed TIPS-Pentacene OFETs

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Polymer nanocomposite dielectric inks based on P(VDF-TrFE)/PMMA/BaTiO₃/Silica were formulated for screen printing. GPTMS-modified BaTiO₃ was incorporated to improve their dielectric properties and fumed silica to achieve good printability of the dielectric inks. Fully-printed TIPS-pentacene OFETs were successfully fabricated using the optimized dielectric ink with 52% BaTiO₃ loading.

15 Fully-additive (vis-a-vis subtractive) printed electronics¹ have attracted much interest within the printed electronics community. The device mobility of fully-printed transistors is in the range which is automatically lower than that of silicon-based transistors.²⁻⁴ Whilst low mobility is a limitation of printed

20 electronics, it is largely complementary to silicon-based electronics, because of its advantages such as low-cost and solution-processable device fabrication. Being able to obtain high capacitance for organic field-effect transistors (OFETs) is important to achieve improving frequency, low operating voltage,

25 and efficient device scalability. The high capacitance can be achieved by using high permittivity dielectric insulator or thin dielectric films. In printed electronics, polymer nanocomposite dielectric materials⁵⁻¹¹ had attracted much attention because they could meet the requirements of good solution processability and

30 mechanical properties of polymers combined with unique electrical properties of nanoparticles. Among all the polymer matrices, PVDF-based fluoropolymers have the advantages of high capacitance, high stability and good water repellency. However, they also have the disadvantages of the leakage current

35 and ferroelectric loss under high electric field due to low volume resistivity. This problem can be overcome by control of fluoropolymer chain conformation or by blending polymers with high volume resistivity into the fluoropolymer.

In this article, novel screen-printable polymer nanocomposite dielectric ink has been successfully formulated for fully-printed OFETs fabrication. This dielectric ink is composed of poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) and

poly(methyl methacrylate) (PMMA) blend as polymer binder, BaTiO₃ as ceramic fillers and fumed silica as viscosity modifier.

45 The surface of the blend polymer contained low density electron traps such as hydroxyl groups, little charge trapping was observed at the interface of the dielectric/semiconductor as well as in the bulk dielectric. High-*k* BaTiO₃ nanoparticles was incorporated into the polymer matrix in order to achieve high capacitance.

50 Moreover, the contribution of the ferroelectric nature of the BaTiO₃ to hysteresis is negligible due to its small particle size in this study.

Experimental section

Dielectric ink formulation

55 P(VDF-TrFE) (70/30, Info Piezotech) and PMMA (*M_w* = 120,000) was mixed with a ratio of 7:3 in 1-methyl-2-pyrrolidinone (NMP). BaTiO₃ powder (<100 nm particle size, Sigma-Aldrich) was first de-agglomerated by Ball Mill overnight and modified by silane coupling agent of 3-glycidoxypropyltrimethoxysilane (GPTMS). BaTiO₃ (1g) and GPTMS (2.325 mL) reacted in a mixture solution of ethanol (2 mL), deionized water (0.3 mL) and HCl (0.3 mL, 0.1 M) at 80 °C overnight in the dark. Thereafter, the modified BaTiO₃ powder was collected by centrifugation at 8000 rpm for 30 min, and the

65 resultant solid was subsequently washed by ethanol and deionized water by centrifugation at 8000 rpm for 30 min, respectively. Finally, the white modified BaTiO₃ powder was dried at 40 °C overnight under vacuum. Fumed silica (0.007 μm, Sigma-Aldrich) as the viscosity modifier was incorporated into the

70 polymer nanocomposite dielectric.

Device Fabrication and Characterization

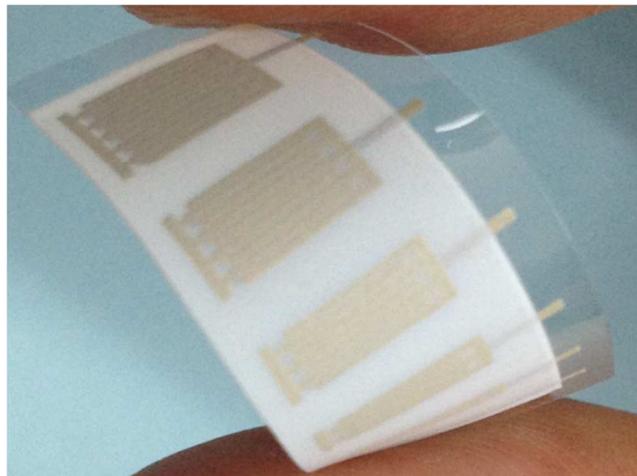


Fig. 1 The optic image of fully-printed OFETs on PET

Fully-printed bottom-gate bottom-contact OFETs were fabricated by screen printing on the polyethylene terephthalate (PET) substrate, as shown in Fig. 1. Silver paste (DuPont) was screen printed on the PET substrate with a speed of 100 mm/s and a pressure of 12 kg and then was cured at 120 °C for 10 min. The formulated dielectric ink was deposited by screen printing with a printing speed of 60 mm/s and a pressure of 8.0 kg and cured at 120 °C for 2 h. The source and drain electrodes were screen printed on the dielectric layer with a speed of 90 mm/s and a pressure of 11 kg, and then cured at 120°C for 10 min. All the printed transistors were cleaned by isopropanol (IPA) and deionized water to remove the contaminants, which were dried at 50 °C for 30 min under vacuum. Subsequently the transistors were treated in PFBT in ethanol (1.4 μL in 1 mL) solution for 1 h, cleaned with ethanol and then dried at 50 °C for 30 min under vacuum. TIPs-pentacene in toluene/anisole solution (80 mg in 2.4 mL/0.6 mL) was deposited on the device by slot die coating, with a speed of 0.3 mm/s and a substrate temperature of 70 °C, and then annealed at 90 °C for 30 min on the hot plate. The electrical characteristics of TIPs-pentacene OFETs using polymer nanocomposite dielectrics were measured using Keithley 4200-SCS under ambient atmosphere. The field-effect mobility of TIPs-pentacene OFETs is extracted using the following equation in the saturation region: $I_D = W/(2L)C\mu(V_G - V_T)^2$. All OFETs have an aspect width/length ratio of 40,000 μm:100 μm.

Results and Discussion

Pristine P(VDF-TrFE) showed ferroelectric properties due to strong dipolar polarization in the crystalline β-phase of the polymer film.¹² Amorphous PMMA was introduced to reduce the P(VDF-TrFE) crystallinity, thus eliminating the hysteresis introduced by the ferroelectric crystalline. Due to high surface energy and tendency to agglomeration, BaTiO₃ powder was first de-agglomerated and modified by silane coupling agent of GPTMS to facilitate well dispersion into the polymer matrix. NMP is favorable for the formulation of dielectric inks for printing due to its good solvency, low volatility, low flammability

and relatively low toxicity. The viscosity of dielectric ink was reduced when adding the GPTMS-modified BaTiO₃ nanoparticles that were suspended in NMP. To further adjust dielectric printability, small amount of fumed silica was used to fine tune the viscosity and printability without degrading ink dielectric properties and adhesion to the substrate. By adjusting the amount of the fumed silica and the solvent, the dielectric ink could form continuous and pinhole-free films on the PET substrate by screen printing. The detailed compositions of polymer nanocomposite dielectric inks of S1 (0%), S2 (22%), S3 (36%) and S4 (52%) with different BaTiO₃ loadings were listed in Table S1 (in Supporting Information). It was noted that the amount of fumed silica was 8% of the dielectric S1, 5% of S2, 4% of S3 and 3% of S4, respectively. With a high concentration of fumed silica above 10%, the formulated dielectric ink could be screen printed, but the dielectric film cracked on the PET substrate after thermal curing at 120 °C. Consequently, the concentration of viscosity modifier should be minimized to achieve good printability and compatibility of dielectric ink with the substrate, which was crucial for the ink formulation of this polymer nanocomposite dielectric. The viscosity of dielectric S1, S2, S3 and S4 was measured to be 11 Pa.s, 11 Pa.s, 14 Pa.s and 15 Pa.s, respectively. Moreover, the dispersions formed with fumed silica were quite stable, remaining unchanged for months.

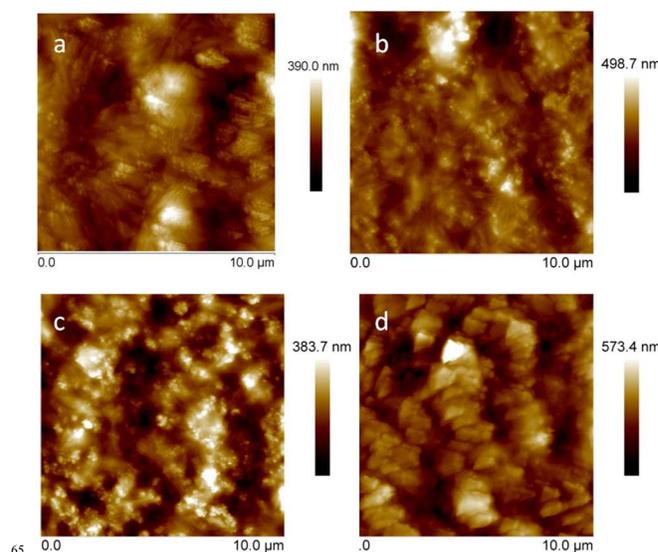


Fig. 2 AFM topographical images of dielectric films deposited by screen printing (a) dielectric S1; (b) S2; (c) S3; and (d) S4.

In order to get insight into the effect of BaTiO₃ loading on the dielectric films, the surface morphology of the screen-printed dielectric films was measured by the tapping mode atomic force microscopy (AFM), as shown in Fig. 2. It was observed that the dielectric S1 exhibited rigid rod-like crystal structure without loading BaTiO₃ into the polymer matrix. With the incorporation of BaTiO₃, the color of the dielectric films on PET substrate changed from transparent to white and the surface morphology changed accordingly. It was observed that the modified

nanoparticles, having an average particle size of 125 nm, were well dispersed in the crystal grains on the surface of the dielectric films of S2 and S3, which indicated that GPTMS-modified BaTiO₃ had good miscibility with the polymer matrix. For S4 with high loading of 52% BaTiO₃, the nanocomposite film still presents good miscibility with no sign of phase separation between nanoparticles and polymer binder (Fig. 2d). In addition, with an increase in BaTiO₃ loading, the surface roughness (R) of the dielectric films was increased, with dielectric S1 of 51 nm, S2 of 64 nm, S3 of 69 nm and S4 of 81 nm, respectively. The 3D AFM images were depicted in Fig. S1 (in Supporting Information)

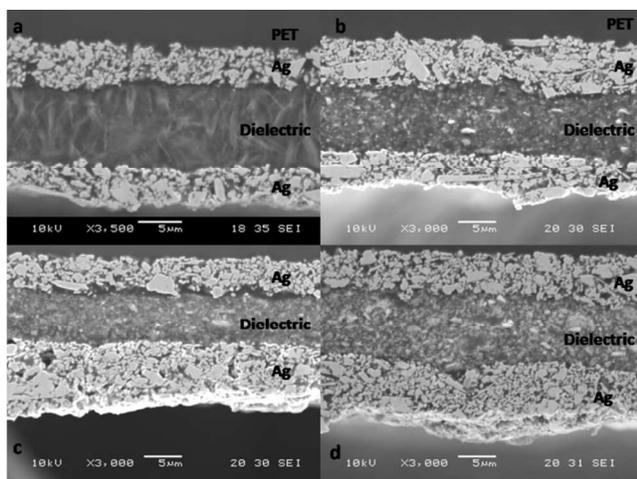


Fig. 3 Cross section SEM micrographs of the polymer nanocomposite dielectric annealed at 120 °C (a) dielectric S1; (b) S2; (c) S3; and (d) S4.

Cross section specimens for scanning electron microscopy (SEM) measurement were prepared by cross section polisher (JEOL IB-09010CP) to investigate the morphology of bulk dielectric films deposited by screen printing. Fig. 3 shows cross section SEM micrographs of dielectric films of S1, S2, S3 and S4. The morphology of the bulk dielectric was consistent through the dielectric thickness, which was in agreement with the surface morphology of the dielectric measured by AFM. With blending amorphous PMMA, the dielectric S1 showed typical rigid rod-like crystal structure, with an average diameter of 280 nm. With an increase in BaTiO₃ loading, the rigid rod-like crystal structure of polymer matrix disappeared in the bulk dielectric film which is typical of nanocomposite films. The dielectric thicknesses of dielectrics S1, S2, S3 and S4 were measured to be 9 µm, 9 µm, 6 µm, 9 µm, respectively.

Table 1 Properties of dielectrics and fully-printed TIPs-pentacene OFETs

Ink	k	R (nm)	V_T^d (V)	I_{on}/I_{off}^d	μ^d (cm ² /Vs)
S1	6.4	51	-1.5	10 ⁴	0.04
S2	6.9	64	-3.5	10 ⁴	0.04
S3	7.9	69	-2.6	10 ⁴	0.04
S4	10	81	-2.5	10 ⁵	0.16

^d: measured at a drain voltage (V_D) of -60 V.

Fully-printed TIPs-pentacene was successfully fabricated on plastic substrate using the formulated dielectric inks. The silver electrodes were treated by the self-assembled monolayer of PFBT to enhance the work function and improve good charge injection. TIPs-pentacene deposited by slot die coating was used as the active semiconductor due to its good crystallization and solution processability. The HOMO level of TIPs-pentacene was -5.3 eV and PFBT-treated Ag had a work function of -5.35 eV. Table 1 tabulates the properties of formulated dielectrics and TIPs-pentacene OFETs using them as gate dielectrics. With an increase in BaTiO₃ loading from 0% to 52%, the dielectric constant was increased from 6.4 to 10 with the capacitance increased from 0.63 nF/cm² to 0.99 nF/cm². The capacitance of the dielectric was obtained from the capacitance-voltage curve with a capacitor area of 1 × 1 cm², as shown in Fig.S2 (in Supporting Information).

It was observed that TIPs-pentacene OFETs with S2 and S3 as the gate dielectrics had small hysteresis under multiple bias sweeping, as shown in Fig. S3 (in Supporting Information). First of all, the hydrophobic surface of the fluoropolymer contained low density of electron traps such as hydroxyl groups, so little charge trapping was observed at the interface of the dielectric/semiconductor as well as in the bulk dielectric. Secondly, GPTMS-modified BaTiO₃ nanoparticles had small particle size, so the degree of ferroelectricity was likely to be too small to carry out the strong $I-V$ hysteresis. Therefore, the good electrical properties make sure that P(VDF-TrFE)-based polymer nanocomposite dielectrics are suitable for ink formulation in printed electronics.

The comparison of the gate leakage current of OFETs using S1 and S2 as gate dielectrics was depicted in Fig. S4 (in Supporting Information). The OFETs using dielectric S1 without BaTiO₃ exhibited an order of magnitude higher leakage current (10⁻⁸ Amp at -60 V gate bias), comparing to the leakage current (10⁻⁹ Amp) obtained from the OFETs using dielectric S2 at the similar operating condition. The low leakage current obtained from OFETs using dielectric S2 was attributed to the good miscibility of modified BaTiO₃ and polymer binder.

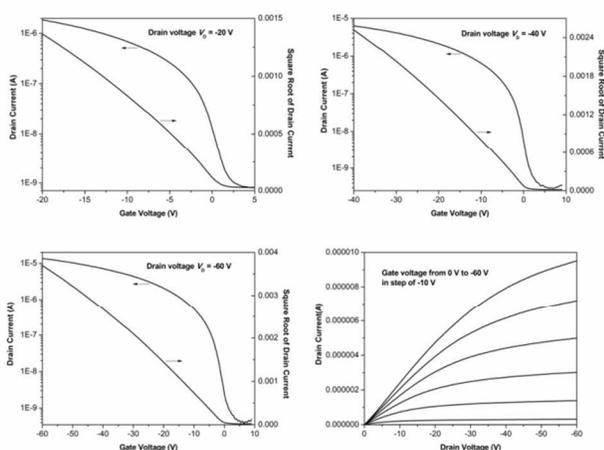


Fig. 4 The characteristics of TIPs-pentacene OFETs using S1 as gate dielectric

The effect of BaTiO₃ loading on the electrical characteristics of TIPs-pentacene OFETs was measured under different drain voltages. As shown in Fig. 4, the transistor using S1 as gate dielectric was switched on at a drain voltage (V_D) of -20 V, but had a low I_{on}/I_{off} of 10^3 ; whereas the transistor exhibited a mobility of $0.04 \text{ cm}^2/\text{Vs}$, having an I_{on}/I_{off} of 10^4 and a threshold voltage (V_T) of -1.5 V at a V_D of -60 V. The transistors using S2 and S3 as gate dielectrics had comparable mobility of $0.04 \text{ cm}^2/\text{Vs}$ and an I_{on}/I_{off} of 10^4 at a V_D of -60 V, as depicted in Fig. S5-S6 (in Supporting Information).

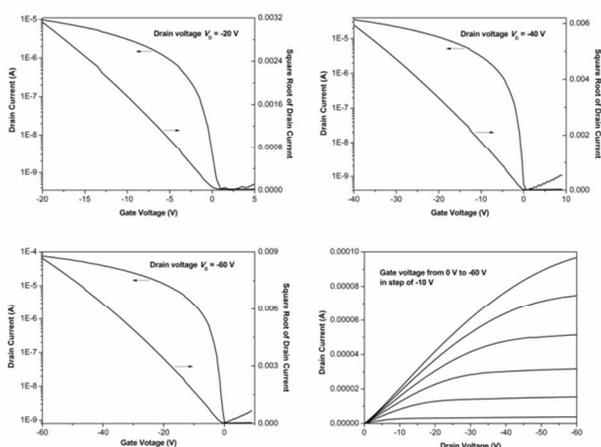


Fig. 5 The characteristics of TIPs-pentacene OFETs using S4 as gate dielectric

In comparison, the device performance was greatly improved when the BaTiO₃ loading was increased to 52% in dielectric S4. Fig. 5 shows the transfer curves of fully-printed TIPs-pentacene OFETs using the dielectric S4 at V_D of -20 V, -40 V and -60 V as well as the I - V curves. Using S4 as gate dielectric, TIPs-pentacene OFETs was operated at a V_D of -20 V, having a mobility of $0.2 \text{ cm}^2/\text{Vs}$, a V_T of -1.1 V and an I_{on}/I_{off} of 10^4 . When measured at a V_D of -40 V, the transistor showed a mobility of

$0.17 \text{ cm}^2/\text{Vs}$ and a V_T of -2.6 V. The transistor exhibited a mobility of $0.16 \text{ cm}^2/\text{Vs}$ and an I_{on}/I_{off} of 10^5 at V_D of -60 V. The value of the mobility is 4 times that of the device using S1 as the dielectric. Moreover, for the dielectric S4 with high BaTiO₃ loading, the leakage current of the transistor remained at 10^{-9} Amp even at high gate bias. Thence, the optimized dielectric ink with BaTiO₃ loading not only improved the capacitance of polymer nanocomposite dielectrics, but also achieved fully-printed OFETs with good device performance.

Conclusions

This methodology of ink formulation aimed to achieve low-voltage operation, so high- k P(VDF-TrFE) was considered as polymer matrix. Low- k PMMA was blended to tune the bulk crystallinity and surface morphology of the dielectric films, thus reducing the amount of the ferroelectric crystalline to avoid hysteresis. Modified BaTiO₃ was loaded into the polymer matrix to achieve high capacitance, low gate leakage current and small hysteresis of OFETs. In addition, the fumed silica as the viscosity modifier endowed its good printability and compatibility of the dielectric ink with the PET substrate. Fully-printed TIPs-pentacene OFETs have been successfully fabricated on the PET substrate using the optimized dielectrics. With GPTMS-modified BaTiO₃ loading of 52%, the transistor can be operated at a low drain voltage of -20 V, having a mobility of $0.2 \text{ cm}^2/\text{Vs}$ and an I_{on}/I_{off} of 10^4 . This dielectric ink is promising for the realization of fully-printed analog and digital printed circuits.

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- J. S. Chang, X. Zhang, T. Ge, J. Zhou, *Organic Electronics*. 2014, **15**, 701-710.
- J. Shi, C. X. Guo, M. B. Chan-Park, C. M. Li, *Adv. Mater.* 2012, **24**, 358.
- J. Chang, T. Ge, and E. Sanchez-Sinencio, *Midwest Symposium on Circuits and Systems*, 2012, 582.
- J. Zhao, Y. Gao, W. Gu, C. Wang, J. Lin, Z. Chen, Z. Cui, *J. Mater. Chem.* 2012, **22**, 20747.

-
- 5 A. Rasul, J. Zhang, D. Gamota, M. Singh, C. Takoudis, *Thin Solid Films*, 2010, **518**, 7024.
- 6 S. Ramesh, B. A. Shutzberg, C. C. Huang, J. Gao, E. P. Giannelis, *Advanced Packaging, IEEE Transactions on*, 2003, **26**, 17.
- 5 7 E. Tuncer, I. Sauers, D. R. James, A. R. Ellis, M. P. Paranthaman, T. Aytu, S. Sathyamurthy, K. L. More, A. Goyal, *Nanotechnology*, 2007, **18**.
- 8 R. N. Das, H. T. Lin, J. M. Lauffer, V. R. Markovich, *Circuit World*, **37**, 38-45.
- 10 9 M. Iijima, M. Sato, I. WuledLenggoro, H. Kamiya, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2009, **352**, 88.
- 10 L. Ramajo, M. M. Reboredo, M. S. Castro, *International Journal of Applied Ceramic Technology*, **7**, 444.
- 15 11 M. Jung, J. Kim, J. Noh, N. Lim, C. Lim, G. Lee, J. Kim, H. Kang, K. Jung, A. D. Leonard, J. M. Tour, G. Cho. *IEEE Transactions on Electron Devices*. 2010, **57**, 571.
- 12 S. W. Jung, K. J. Baeg, S. M. Yoon, I. K. You, J. K. Lee, Y. S. Kim, Y. Y. Noh, *J. Appl. Phys.* 2010, **108**, 102810.
- 20 13 N. Stingelin-Stutzmann, *Nat. Mater.* 2008, **7**, 171.
- 14 J. J. Chang, C. Y. Chi, J. Zhang, J. S. Wu, *Adv. Mater.* 2013, **25**, 6442.
- 15 S. K. Park, T. N. Jackson, J. E. Anthony, D. A. Mourey, *Appl. Phys. Lett.* 2007, **91**, 063514.
- 25 16 J. S. Brooks, D. L. Eaton, J. E. Anthony, S. R. Parkin, J. W. Brill, Y. Sushko, *Curr. Appl. Phys.* 2001, **1**, 301.
- 17 X. Li, W. T. T. Smaal, C. Kjellander, B. Van Der Putten, K. Gualandris, E. C. P. Smits, J. Anthony, D. J. Broer, P. W. M. Blom, J. Genoe, G. Gelinck, *Org. Electron.: physics, materials, applications*, 2011, **12**, 1319.
- 30 18 M. K. Kilaru, J. Heikenfeld, G. Lin, J. E. Mark, *Appl. Phys. Lett.* 2007, **90**, 212906