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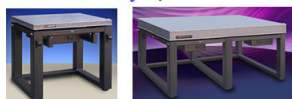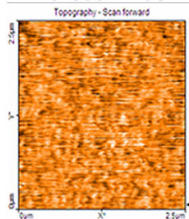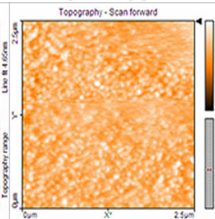
Enhanced carrier mobility and electrical stability of n-channel polymer thin film transistors by use of low-k dielectric buffer layer

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Insertion of a low-k polymer dielectric layer between the SiO_2 gate dielectric and poly(benzobisimidazobenzophenanthroline) (BBL) semiconductor of n-channel transistors is found to increase the field-effect mobility of electrons from 3.6×10^{-4} cm^2/Vs to as high as 0.028 cm^2/Vs. The enhanced carrier mobility was accompanied by improved multicycling stability and durability in ambient air. Studies of a series of eight polymer dielectrics showed that the electron mobility increased exponentially with decreasing dielectric constant, which can be explained to result from the reduced energetic expense of charge-carrier/dipole interaction. © 2011 American Institute of Physics. [doi:10.1063/1.3655680]

Development of highly stable n-channel organic thin film transistors (OTFTs) fabricated by a solution-based processing has been one of the main challenges in organic electronics.[1–5] Since engineering of the gate insulator is one of the promising means to enhance the performance of the OTFTs,[2] the properties of the polymer dielectric layer affecting the performance of OTFTs have been studied by varying the chemical functionality,[6] roughness,[7] viscoelasticity,[8] surface energy,[9] and dielectric constant (k).[10–12] These properties of the dielectric layer appear to affect the device performance by influencing film growth and morphology as well as through energetic interactions between charge carriers and the dielectric medium. However, studies of effects of the polymer buffer layer on charge transport in organic semiconductors have been largely limited to vacuum-deposited small molecules, including pentacene,[6–9,12–14] perylenetetracarboxydiimide,[15] and fullerene.[16] Energetic, viscoelastic, and topographic properties of the buffer layer inevitably affect the morphology of the organic semiconductor during film deposition, and thus the deconvolution of various factors affecting charge transport remains challenging. Systems with sequential solution-based deposition of dielectrics and organic semiconductors have not been well-studied because most of the insulating polymers, except for a few crosslinked ones, are highly soluble in organic solvents and are easily destroyed by a solution of the organic semiconductor. Also, the scarcity of n-type polymer semiconductors[1] hinders detailed investigation of electron transporting in n-channel OTFTs. Although top-gate approach has been proposed and can be used to avoid such limitations, the possibilities of interfacial intermixing and morphological changes during solution-processing remain.[5,10,11]

In this letter, we report an investigation of the effect of low-k polymer dielectric buffer layer of the gate insulator on the charge transport in n-channel polymer thin film transistors (Fig. 1). It is found that the field-effect mobility of electrons in ladder-type poly(benzobisimidazobenzophenanthroline) (BBL) thin film transistors increased exponentially with

decreasing dielectric constant of the polymer dielectric buffer layer. The n-type polymer semiconductor BBL, whose molecular structure is shown in Fig. 1(b), offered a unique opportunity to perform the present experiments by virtue of its solution processability from methanesulfonic acid (MSA) at room temperature,[4,17–19] which is orthogonal to the organic solvents (toluene, mesitylene, and chlorobenzene) from which the polymer dielectric layers were spin-coated.

Various polymer dielectrics, including polystyrene (PS; $k = 2.55$),[20] poly(α-methylstyrene) (PαMS; $k = 2.6$),[20] poly(2-vinylnaphthalene) (P2VN; $k = 2.6$),[13] poly(vinylcarbazole) (PVK; $k = 3.0$),[20] poly(vinylchloride) (PVC; $k = 3.4$),[20] poly(vinylbenzyl chloride) (60/40 mixture of 3- and 4-isomers; PVBC; $k = 2.9$),[21] cyclic olefin copolymer (ethylene-norbornene copolymer; COC; $k = 2.35$),[22] and crosslinked benzocyclobutene (BCB; $k = 2.65$),[23] were used to fabricate the polymer dielectric buffer layers (Fig. 1(c)) and thus to study the effects of the dielectric constant of the buffer layer on charge transport. Absence of alkyl side-chains on the BBL backbone is also advantageous to investigate the effects of an adjacent dielectric material without the convoluted effects of the side-chains. The effects of roughness, viscoelasticity, and surface energy of the polymer buffer layer can be minimized during film deposition. Therefore, consideration of domain growth[8,9] is excluded from the investigation of dielectric/electron interactions in OTFTs.

OTFTs with top-contact and bottom-gate geometry were made on a heavily n-doped silicon wafer with a 200 nm-thick SiO_2. A polymer buffer layer was deposited by spin-coating the solution (COC, PS, PαMS, P2VN, and PVBC in toluene; BCB in mesitylene; PVK in chlorobenzene; and PVC in 1,2-dichlorobenzene) on top of a plasma-cleaned substrate and dried under vacuum at 60 °C. The film thickness and root-mean-square roughness of the polymer buffer layers were 3.7–75.2 nm and 0.2–0.7 nm, respectively, measured by atomic force microscopy. The capacitance per unit area of the gate dielectric was in the range of 12.1–16.8 nF/cm^2, measured from a metal-insulator-metal (MIM) structure (n^{++}-Si/SiO$_2$/polymer/Au) or calculated by the dielectric constant and

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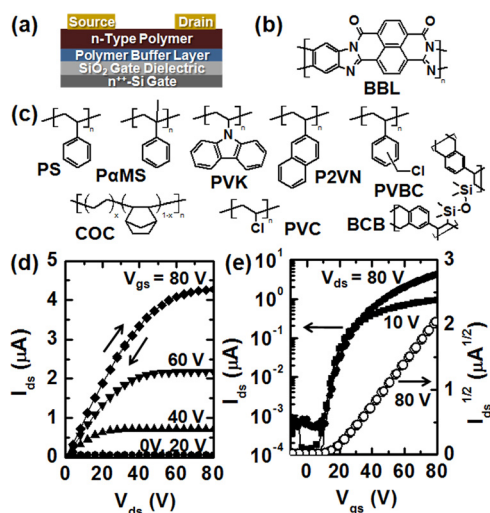
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FIG. 1. (Color online) (a) Schematic cross-section of *n*-channel OTFT with a dielectric polymer buffer layer. (b) Molecular structure of the *n*-type polymer semiconductor, BBL. (c) Molecular structures of the dielectric polymers studied. (d) Output and (e) transfer characteristics of *n*-channel BBL transistors with a PS buffer layer.

thickness of SiO_2 and the buffer layer. The measured and calculated capacitances were in good agreement within 5%. The static contact angle of water on the polymer buffer layers was in the range of 82°–96°, which is much higher than that on plasma-cleaned SiO_2 without any buffer layer ($\sim$0°). The *n*-channel semiconductor, BBL, was spin-coated from a solution in MSA onto the substrate in air and immediately washed by dipping the film in water or methanol for 4–5 times over 2–3 h to remove the acid solvent.[18] The BBL film (20–40 nm thick) was dried under vacuum at 60 °C for 8–12 h and annealed at 150 °C for 10 min under argon environment. The transistors were finished by depositing 40 nm-thick gold source/drain electrodes through a shadow mask to define the transistor channel (width/length = 1000 μm/100 μm). The OTFTs were characterized at room temperature under nitrogen by using an HP4145B (or in ambient air by using a Keithley 4200) semiconductor parameter analyzer.

Output and transfer characteristics of the BBL transistors with a PS buffer layer showed clear current modulation and saturation, as shown in Fig. 1(d) and 1(e). The on/off current ratios were in the range of 10^3–10^4. Forward and backward scans are overlaid to emphasize the negligible hysteresis of the devices. Other polymer buffer layers also showed similar current (I)–voltage (V) characteristics with negligible hysteresis. In order to quantify the performance of OTFTs with various polymer dielectric buffer layers, the field-effect electron mobility was calculated from the saturation region of I–V characteristics at $V_{ds} = 80$ V. The mobility as high as 0.028 cm^2/Vs was recorded from the devices with a PS buffer layer. The average mobility of 6–30 devices was 0.018 ($\pm$0.004), 0.020 ($\pm$0.002), and 0.016 ($\pm$0.006) cm^2/Vs for PS, COC, and BCB buffer layers, respectively. These mobilities are 44–56 times enhanced compared to the electron mobility of control devices with a bare SiO_2 as the dielectric layer ($3.6 \times 10^{-4} \pm 0.0002$ cm^2/Vs). OTFTs with PαMS and P2VN have average mobility of 0.017 ($\pm$0.002) and 0.013 ($\pm$0.002) cm^2/Vs, respectively. Unlike the low-*k* ($k < 2.7$) polymer dielectrics, devices with PVK, PVBC, or PVC buffer layer

had a rather low average mobility in the range of 5.2×10^{-4}–5.8×10^{-3} cm^2/Vs.

Fig. 2(a) shows the field-effect electron mobility (μ) as a function of the dielectric constant (*k*) of the polymeric buffer layer. The electron mobility is described by $\mu = A \exp(-B k)$, i.e., the mobility increased exponentially with decreasing dielectric constant. Such a dependence of the mobility on the dielectric constant of the polymeric buffer layer can be explained by the energetic expense caused by the interaction between charge-carriers in the organic semiconductor and dipoles at the adjacent dielectric layer.[10] A similar relationship, i.e., increase in μ with decreasing *k*, has been previously reported from amorphous *p*-type polymer semiconductors[10] and a rubrene single crystal,[24] but it is contradictory to the report on a polymer semiconductor with long alkyl side-chains where the carrier mobility was independent of *k*.[5,11] Since the former two organic semiconductors lack side-chains, similar to BBL, the contradictory result of the latter is likely from the screening effect of alkyl chains (see below).

The exponential dependence of carrier mobility has been seen in various charge transport models of organic semiconductors, such as the Arrhenius-type thermally activated transport model ($\mu = \mu_{A0}\exp(-E_A/k_BT)$) and the Gaussian density of states model ($\mu = \mu_{G0}\exp(-(\sigma/k_BT)^2)$).[2,10] Significant interaction between charge-carriers and dipoles can be considered to increase activation energy (E_A) or energetic disorder expressed by the width of Gaussian distribution (σ). The observed effect of the dielectric constant of the buffer layer on electron mobility is described by $\mu = A \exp(-B k)$. The pre-exponential factor *A* and the constant *B* define how highly the mobility depends on the dielectric constant at room temperature. Linear fit (Fig. 2(a)) of the semi-log plot of the mobility (μ) vs dielectric constant (*k*) resulted in $A = 39.9$ cm^2/Vs and $B = 3.07$ at room temperature. This result suggests that the room-temperature field-effect mobility may be as high as 1.85 cm^2/Vs in a device with vacuum (or air) as the dielectric layer ($k = 1$).

We have studied the dependence of the mobility on the thickness of the buffer layer by varying the PS buffer thickness from 3.7 nm to 75.2 nm, so as to estimate a minimum thickness of a buffer layer that affects charge transport in organic semiconductors. The electron mobility was essentially identical throughout the range of buffer layer thickness (Fig. 2(b)), suggesting that the influence of a dielectric layer on charge transport in organic semiconductor is localized within a short range from the heterointerface of the semiconductor/insulator system. Analytical modeling on amorphous *p*-type
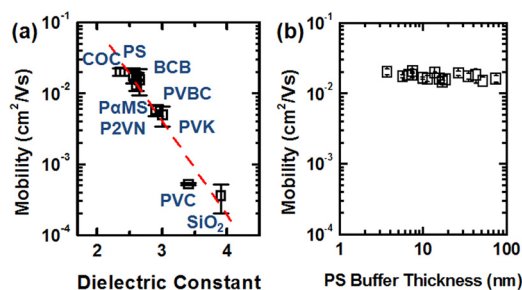

FIG. 2. (Color online) (a) Field-effect electron mobility as a function of dielectric constant of the polymer dielectric buffer layer. Dashed line is a fitting equation: $\mu = A \exp(-B k)$. (b) Electron mobility as a function of thickness of the PS buffer layer.

polymer semiconductor has shown that the range of static dipolar disorder can be even less than 1 nm.[25] This explains why some polymer semiconductors with alkyl side-chains show dielectric-constant independence of the carrier mobility.[5,11] Our result shows that the low-k buffer layer could be as thin as a few nanometers in a high-k/low-k multilayer gate systems for high-performance, low-voltage operation.[26] We note that the buffer layers have similarly low surface roughness (0.2–0.7 nm), precluding us from finding any correlation between the mobility and roughness.

The polymer dielectric buffer layer not only enhances field-effect mobility but also stabilizes the electrical characteristics. The BBL transistors without any buffer layer suffered from large hysteresis and voltage shift, as shown in overlays of 100 cycles (Fig. 3(a)). On the other hand, the hysteresis was reduced to 0–4 V by inserting a polymer buffer layer. The largest hysteresis of 4 V was observed from devices with PVK as a buffer layer. The multicyclic voltage shift was also reduced to 0 V as exemplified by the transistors with a PS buffer layer that show identical characteristics of 1000 cycles of gate voltage sweep between 0 V and 80 V at $V_{ds} = 80$ V, recorded for 7 h (Fig. 3(b)). The stable cyclic operation is considered to be from the absence of charge trapping sites, such as carbonyl and hydroxyl groups, in the buffer layer.[6,16] Impurities such as mobile ions in SiO_2 are also effectively screened by the polymer buffer layer. Combination of high-durability of BBL in air[4,17–19] and high-stability of OTFTs with polymer buffer layer results in the remarkable air-stability of the n-channel devices in terms of field-effect mobility and threshold voltage (Fig. 3(c)). Although initial changes of the mobility and the threshold voltage were

observed as the BBL OTFTs were taken out from inert conditions to ambient air, the mobility and the threshold voltage are stabilized to $\sim 2 \times 10^{-3}$ cm^2/Vs and ~ 35 V, respectively, when stored and periodically tested in air over 80 days.

In conclusion, we have showed that the performance of solution-processed n-channel polymer OTFTs, in terms of electron mobility and electrical stability, can be significantly enhanced by applying a polymer dielectric buffer layer. The field-effect electron mobility has been increased by two orders of magnitude by applying a low-k polymer buffer layer. A systematic study shows that the electron mobility exponentially decays as the dielectric constant of the buffer layer increases. In the limit of air or vacuum as the dielectric buffer layer ($k = 1$), the room temperature electron mobility of the BBL OTFTs is projected to be as high as 1.85 cm^2/Vs. This finding emphasizes the importance of energetic nature of dielectric/semiconductor interfaces for understanding electron transport in organic semiconductors.
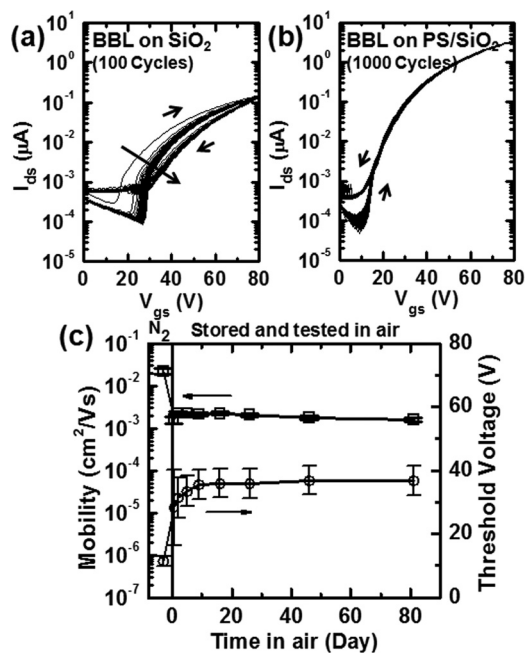
FIG. 3. Multicyclic stability and air-durability of *n*-channel OTFTs: Overlays of transfer curves of BBL OTFTs (a) without and (b) with a 43.0 nm-thick PS buffer layer. V_{ds} was fixed at 80 V for both cases. (c) Electron mobility and threshold voltage of BBL transistors with a 17.5 nm-thick BCB buffer layer as a function of time in air. Devices were stored and periodically characterized in air for durability test.

[1] Z. Bao, Adv. Mater. **12**, 227 (2000).
[2] H. Sirringhaus, Adv. Mater. **17**, 2411 (2005).
[3] G. Gelinck, P. Heremans, K. Nomoto, and T. D. Anthopoulos, Adv. Mater. **22**, 3778 (2010).
[4] A. Babel and S. A. Jenekhe, J. Am. Chem. Soc. **125**, 13656 (2003).
[5] Z. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dotz, M. Kastler, and A. Facchetti, Nature **457**, 679 (2009).
[6] M.-H. Yoon, C. Kim, A. Facchetti, and T. J. Marks, J. Am. Chem. Soc. **128**, 12851 (2006).
[7] S. E. Fritz, T. W. Kelley, and C. D. Frisbie, J. Phys. Chem. B **109**, 10574 (2005).
[8] C. Kim, A. Facchetti, and T. J. Marks, Adv. Mater. **19**, 2561 (2007).
[9] H. Yang, S. H. Kim, L. Yang, S. Y. Yang, and C. E. Park, Adv. Mater. **19**, 2868 (2007).
[10] J. Veres, S. D. Ogier, S. W. Leeming, D. C. Cupertino, and S. M. Khaffaf, Adv. Funct. Mater. **13**, 199 (2003).
[11] N. Zhao, Y. Y. Noh, J. F. Chang, M. Heeney, I. McCulloch, and H. Sirringhaus, Adv. Mater. **21**, 3759 (2009).
[12] Y. Jang, D. H. Kim, Y. D. Park, J. H. Cho, M. Hwang, and K. Cho, Appl. Phys. Lett. **87**, 152105 (2005).
[13] G. Nunes, S. G. Zane, and J. S. Meth, J. Appl. Phys. **98**, 104503 (2005).
[14] Y. Wang, O. Acton, G. Ting, T. Weidner, H. Ma, D. G. Castner, and A. K.-Y. Jen, Appl. Phys. Lett. **95**, 243302 (2009).
[15] J. Jang, S. Nam, D. S. Chung, S. H. Kim, W. M. Yun, and C. E. Park, Adv. Funct. Mater. **20**, 2611 (2010).
[16] X. H. Zhang, B. Domercq, and B. Kippelen, Appl. Phys. Lett. **91**, 092114 (2007).
[17] A. Babel, Y. Zhu, K. F. Cheng, W. C. Chen, and S. A. Jenekhe, Adv. Funct. Mater. **17**, 2542 (2007).
[18] F. S. Kim, E. Ahmed, S. Subramaniyan, and S. A. Jenekhe, ACS Appl. Mater. Interface **2**, 2974 (2010).
[19] A. L. Briseno, F. S. Kim, A. Babel, Y. Xia, and S. A. Jenekhe, J. Mater. Chem. **21**, 16461 (2011).
[20] J. E. Mark, *Polymer Data Handbook* (Oxford University Press, New York, 1999).
[21] A. Abbotto, L. Beverina, S. Bradamante, A. Facchetti, C. Klein, G. A. Pagani, M. Redi-Abshiro, and R. Wortmann, Chem. Eur. J. **9**, 1991 (2003).
[22] T. C. K. Yang, S. H. Y. Tsai, S.-F. Wang, and C.-C. Juan, Compos. Sci. Technol. **62**, 655 (2002).
[23] M. E. Mills, P. Townsend, D. Castillo, S. Martin, and A. Achen, Microelectron. Eng. **33**, 327 (1997).
[24] A. F. Stassen, R. W. I. d. Boer, N. N. Iosad, and A. F. Morpurgo, Appl. Phys. Lett. **85**, 3899 (2004).
[25] T. Richards, M. Bird, and H. Sirringhaus, J. Chem. Phys. **128**, 234905 (2008).
[26] D. K. Hwang, C. S. Kim, J. M. Choi, K. Lee, J. H. Park, E. Kim, H. K. Baik, J. H. Kim, and S. Im, Adv. Mater. **18**, 2299 (2006).