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Solution-Based TiO_2−Polymer Composite Dielectric for Low Operating Voltage OTFTs

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Abstract: The cross-linking reaction of a TiO_2−polymer composite (TPC) dielectric with poly(4-vinyl phenol) (PVP), a TiO_2 precursor, and poly(melamine-*co*-formaldehyde) is demonstrated: We suggest that the dense chemical structure of TPC is caused by the alkoxyl group of the PVP cross-linker, poly(melamine-*co*-formaldehyde) methylated/butylated, reacted with the hydroxyl group of the PVP and the ligands of the TiO_2 precursor.

Organic thin film transistors (OTFTs), which are appropriate for flexible and lightweight devices compared with traditional inorganic electronics, have considerable potential for printable electronics.[1] Also, OTFT-based electronics are very attractive because they are simple and cost efficient with a high throughput of solution processing and the printing method. However, there are several challenges regarding OTFTs, such as a high operating voltage induced by the low charge carrier mobility of organic semiconductors and the low dielectric property of the organic gate dielectric.[2] The low operating voltage is essential for various OTFTs applications, such as portable displays,[3] smart cards,[4] and radio frequency identification tags.[5] Furthermore, patchable electronics[6] such as smart patches[7] and smart textiles[8] must be operated at low voltages because they are worn on the human body. To operate at low voltage, OTFTs must have an organic insulator with a high dielectric constant. In previous research, various polymer dielectric materials, such as poly(4-vinyl phenol) (PVP),[9] poly(methylmethacrylate) (PMMA),[10] poly(styrene) (PS),[11] poly(perfluorobutenylvinylether) (CYTOP),[12] and poly(acrylic acid) (PAA)[13] have been studied by many research groups. However, polymer materials are not appropriate for use in low voltage applications due to their low dielectric constant (K). In order to overcome this problem, various nanocomposite dielectrics, including inorganic nanoparticles with a high dielectric constant (K), have been studied.[14−16] However, nanocomposite dielectrics in OTFTs have not been shown to have a surface that allows well-aligned organic semiconductor growth, resulting in a low on/off ratio and low carrier mobility in the low voltage range. Furthermore, according to the increase of inorganic particles in nanocomposite materials, the dielectric layer shows high leakage currents because high K materials can generate a high leakage current path.[17]

In OTFTs, the surface of the dielectric layer is important for effective performance because it allows for a conducting channel in the interface between the dielectric layer and semiconductors. In the case of deposition of small semiconductor molecules, such as pentacene, molecular orientation and grain morphology depend strongly on the surface roughness and energy of the underlying film. The low surface energy of the dielectric layer allows the vertical growth of pentacene molecules. As the hole can easily be moved in the vertical direction of pentacene molecules, these vertical alignments of pentacene enhance mobility in OTFTs.[18] In order to decrease the high surface energy of the dielectric−semiconductor interface, the nanocomposite dielectric layer has been deposited by the polymer capping on inorganic materials. However, in this case, the transistors were not operated successfully in a low voltage range due to insufficient dielectric properties caused by polymer capping.

In this study, we have introduced the TiO_2−polymer composite (TPC) gate insulator to overcome the problems discussed above. The TPC is composed of a TiO_2 precursor (titanium(IV) butoxide and acetyl acetone) and poly(4-vinylphenol) (PVP) solution (PVP, poly(melamine-*co*-formaldehyde) methylated/butylated and propylene glycol methyl ether acetate (PGMEA) solvent). As this TPC composite dielectric layer can be easily deposited by a simple solution process and exhibits a considerably low surface energy, it generates a smooth and hydrophobic surface that allows the uniform vertically oriented growth of small semiconductor molecules and closely packed grains between crystal domains. Also, the TiO_2 precursor induces an enhanced dielectric constant compared with the dielectric constant of pristine PVP. As this enhanced dielectric property leads to the increased drain current at a low operating voltage, the OTFTs including this TPC composite dielectric layer can be successfully operated at a low operating voltage. Furthermore, this homogeneous TiO_2−polymer composite solution is stable in ambient conditions, and it was easily applied in the fabrication of OTFTs. As a result, the OTFTs with a TPC dielectric layer exhibited the better transistor performance with an increased on/off ratio, an increased mobility, and a low subthreshold voltage at a low operating voltage compared to the performance of OTFTs that include a pristine PVP polymer dielectric.

The TPC dielectric made from a composite solution of a TiO_2 precursor and PVP (see the Supporting Information) was spin-casted, and the result was a single layer with reddish-orange color. A few minutes after being completely mixed, the TiO_2 precursor solution and the PVP solution for the TPC dielectric turned into gelatin as a result of the cross-linking reaction of poly(melamine-*co*-formaldehyde) methylated/butylated (cross-linker) and the TiO_2 precursor. This gelatin was observed by the naked eye and was transparent with a reddish-orange color. Solvents, including a hydroxyl group, can dissolve the gelatin resulting from the cross-linkable PVP solution and the TiO_2 precursor solution in order to make a homogeneous solution phase with low viscosity. We conducted dissolving tests for various solvents, and the results are summarized in Figure S2. The TPC gelatin can be dissolved in ethanol and 2-propanol, including a hydroxyl group, and was

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converted into a homogeneous solution phase (see supporting Table S1). In this study, we used ethanol to transform the TPC gelatin to the transparent solution phase. As we introduced a complete solution phase composite including an inorganic precursor that can be easily used in the spin-coating process, they show good surface properties, such as extremely low surface roughness.

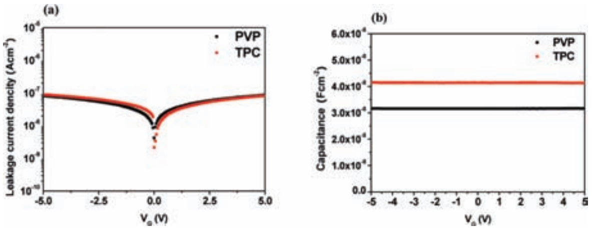

Figure 1. (a) Leakage current density and (b) capacitance of a cross-linked PVP and TPC dielectric layer (Operating voltage: −5 V) .

The leakage currents of TPC and PVP thin films as a gate insulator were measured using current−voltage measurements respectively, as shown in Figure 1a. The leakage current of the TPC gate insulator at ±5 V was about 10^{-7} A cm^{-2}, which is the same as that of the pristine PVP gate insulator. The gate leakage currents of the TPC gate insulator were very low due to the dense chemical structure of TPC induced by cross-linking between poly(melamine-*co*-formaldehyde) methylated/butylated and titanium(IV) butoxide chemically reacted with acetyl acetone. We presume the alkoxyl group of the PVP cross-linker, poly(melamine-*co*-formaldehyde) methylated/butylated, reacted with the hydroxyl group of the PVP and the ligands of the TiO_2 precursor and that this chemical cross-linking generated the dense structure. Although inorganic TiO_2 induces high leakage currents,[17] this TPC that includes a TiO_2 precursor showed a considerable low leakage current compared to the pristine PVP polymer due to the dense chemical structure. Otherwise, the capacitance of the TPC thin film is higher than that of the pristine PVP dielectric layer because of the high dielectric property of TiO_2 composited with PVP. Figure 1b shows the capacitance of the TPC and pristine PVP dielectric layer.

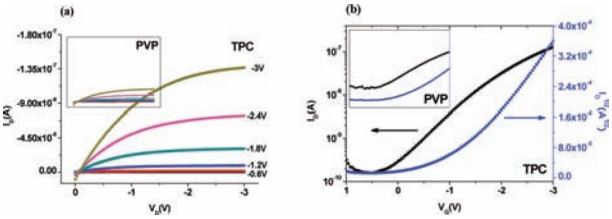

Figure 2. (a) Output and (b) transfer characteristics of OTFTs with TPC thin film as a dielectric layer. Inset images: (a) Output and (b) transfer characteristics of OTFTs with pristine PVP thin film as a dielectric layer (channel length, 100 μm; channel width, 1000 μm; source−drain bias, −3 V).

The performances of the transistor including the TPC and pristine PVP thin films as a gate insulator are indicated by the output characteristics as shown in Figure 2a and inset image, respectively, at −3 V. Although the dielectric constant ($K = 5.2$) of the TPC thin film is not a remarkably high value, this TPC dielectric layer sufficiently improves the output drain current of OTFTs in a low-voltage range. In order to compare the performance of the dielectric layer, the transfer characteristics of OTFTs with a TPC dielectric (Figure 2b) and pristine PVP dielectric (the inset image of Figure 2b) were measured. The on/off ratio of the OTFTs with the TPC dielectric layer was deduced from the transfer characteristics (I_D-V_G) (Figure 2b) and was around ~10^3. The calculated charge carrier mobility of OTFTs with a TPC dielectric was 0.105 cm^2 V^{-1} s^{-1}, while the mobility in OTFTs with a pristine PVP dielectric layer was 0.036 cm^2 V^{-1} s^{-1}. Generally, carrier mobility is dependent on the capacitance of the gate insulator and is affected by the pentacene molecule alignment or morphology. In previous papers,[17] the mobility in OTFTs improved as a result of changing the surface energy of the dielectric layer using surface treatments with self-assembled monolayers such as octadecyltrichlorosilane(OTS). The structures of the TPC surface enhance the charge carrier mobility of transistors as well as the vertical alignment of pentacene molecules induced by low surface energy (see supporting Figure S3). Also, it is well-known that OTFTs with dielectrics that include inorganic nanoparticles have sometimes exhibited electrical instabilities, such as hysteresis, due to the interface defects of nanoparticles.[19] In this study, however, as the TPC dielectric was cross-linked completely with both the TiO_2 precursor and PVP polymer, there was little hysteresis (see supporting Figure S4). The performance of OTFTs with a TPC dielectric layer improved compared to that of OTFTs with a pristine PVP dielectric layer, as summarized in Table 1.

Table 1. Electrical Properties of Cross-Linked Pristine PVP and TPC Composite Film As a Dielectric Layer, Respectively (Operating Voltage: −3 V)

Dielectric materials	Mobility (cm^2 V^{-1} s^{-1})	Threshold Voltage (V_T)	On/off ratio	Subthreshold Swing (V/decade)	Thickness (nm)	Dielectric constant
PVP	0.036	−0.5	5.2×10^1	1.65	110	3.9
TPC	0.105	−0.8	~10^3	0.98	110	5.2

In summary, we introduced a composite polymer dielectric (TPC) layer that included high *K* TiO_2 for low-operating voltage OTFTs. The dielectric properties of TPC, which is composed of PVP, a cross-linker, and a TiO_2 precursor, were enhanced due to the dense chemical structure of the polymer (PVP) and high *K* materials (TiO_2 precursor). This TPC dielectric can easily be used in solution processes, such as spin-casting, and showed good stability in ambient conditions, air environments, and moisture conditions. The TPC thin film as a dielectric layer could sufficiently hinder leakage currents and successfully operate in low-voltage conditions, such as −3 V. Furthermore, the TPC dielectric layer exhibited enhanced performance characteristics, such as on/off ratio, mobility, and subthreshold swing, compared with the pristine PVP dielectric. Although this device showed a low mobility value because of intrinsic organic semiconductor limitation, it operated well at a low voltage bias with considerable and remarkable performance. We conclude that the TPC dielectric, TiO_2−polymer composite dielectric, is quite promising as a dielectric layer in advanced flexible OTFTs.

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Supporting Information Available: Device structure, hysteresis, the properties of TPC surface, experimental preparation for TPC solution and device fabrication, and complete refs 3, 5, and 7. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Forrest, S. R. *Nature* **2004**, *428*, 911–918.
(2) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science.* **2000**, *290*, 2123–2126.
(3) Sheraw, C. D.; West, J.; et al. *Appl. Phys. Lett.* **2002**, *80*, 1088–1090.
(4) Fix, W.; Ullmann, A.; Ficker, J.; Clemens, W. *Appl. Phys. Lett.* **2002**, *81*, 1735–1737.
(5) Baude, P. F.; Theiss, S. D.; et al. *Appl. Phys. Lett.* **2003**, *82*, 3964–3966.
(6) Park, J.; Kim, J.; Lee, S.; Bang, J.; Kim, B. J.; Kim, Y. S.; Cho, J. *J. Mater. Chem.* **2009**, *19*, 4488–4490.
(7) Someya, T.; Sakurai, T.; et al. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 12321–12325.
(8) Maccioni, M.; Orgiu, E.; Cosseddu, P.; Locci, S.; Bonfiglio, A. *Appl. Phys. Lett.* **2006**, *89*, 143515.
(9) Byun, H. S.; Xu, Y.-X.; Song, C. K. *Thin Solid Films.* **2005**, *493*, 278–281.
(10) Angelis, F. D.; Cipolloni, S.; Mariucci, L.; Fortunato, G. *Appl. Phys. Lett.* **2005**, *86*, 203505.
(11) Yoon, M.-H.; Yan, H.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 10388–10395.
(12) Umeda, T.; Kumaki, D.; Tokito, S. *Org. Electro.* **2008**, *9*, 545–549.
(13) Lim, S. H.; Kim, J.; Lee, S.-g.; Kim, Y. S. *Chem. Commun.* **2010**, *46*, 3961–3963.
(14) Chen, F.-C.; Chu, C.-W.; He, J.; Yang, Y.; Lin, J.-L. *Appl. Phys. Lett.* **2004**, *85*, 3295–3297.
(15) Maliakal, A.; Katz, H.; Cotts, P. M.; Subramoney, S.; Mirau, P. *J. Am. Chem. Soc.* **2005**, *127*, 14655–14662.
(16) Jung, C.; Maliakal, A.; Sidorenko, A.; Siegrist, T. *Appl. Phys. Lett.* **2007**, *90*, 062111.
(17) Kim, C.-H.; Bae, J.-H.; Lee, S.-D.; Choi, J. S. *Mol. Cryst. Liq. Cryst.* **2007**, *471*, 147–154.
(18) Park, Y. D.; Lim, J. A.; Lee, H. S.; Cho, K. *Materialstoday.* **2007**, *10*, 46–54.
(19) Faber, H.; Burkhardt, M.; Jedaa, A.; Kalblein, D.; Klauk, H.; Halik, M. *Adv. Mater.* **2009**, *21*, 3099–3014.

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