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All-Inkjet-Printed Organic Thin-Film Transistors with Silver Gate, Source/Drain Electrodes

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We report high-performance all-inkjet-printed organic thin-film transistors (OTFTs), where inkjet-printed silver electrodes, cross-linked poly(4-vinylphenol) (PVP) and 6,13-bis(triisopropylsilyl)ethynyl pentacene (TIPS-pentacene) were used as gate/source/drain electrodes, a gate dielectric layer and an active semiconductor layer, respectively. To evaluate quality of the active semiconductor layer, we also fabricated OTFTs by using spin-coating and drop-casting methods for TIPS-pentacene layer on the inkjet-printed PVP gate dielectric layer. Comparable TFT electrical performances were obtained and well-crystallized TIPS-pentacene layer was formed for all cases. All TIPS-pentacene OTFTs show lower sub-threshold swing values than OTFTs with an evaporated pentacene active semiconductor layer on the inkjet-printed PVP gate dielectric layer. By using optimized inkjet-printing conditions, we obtained mobility of $0.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off ratio of 10^4 for all-inkjet-printed OTFT.

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1. Introduction

Recently, organic thin-film transistors (OTFTs) have attracted much attention for large area, low-temperature flexible electronics application, and their performance has improved significantly by designing good organic materials and optimizing fabrication conditions.^{1–3)} In addition, in order to further reduce the fabrication cost and to further simplify the fabrication process, a direct inkjet-printing process has been widely used in ultra-low-cost, flexible, large-area electronics applications. Since the direct inkjet-printing process can be easily adapted to TFT fabrication process, optimization of the printing conditions including substrate surface energy, ink-jetting control signals, thermal annealing procedure and ink formulation have been studied a lot to improve OTFT performance.^{4,5)}

However, in most cases, inkjet-printing process has been typically applied to formation of source/drain electrodes or an active semiconductor layer in a bottom contact TFT structure because there are, in general, limitations in reliability, resolution, available material, surface roughness of the inkjet-printed layer and adhesion between inkjet-printed layers.^{5–8)} Therefore, although all-inkjet-printed devices have been reported only recently,^{9,10)} electrical performances were relatively poor in comparison with the conventionally fabricated OTFTs using a vacuum or a spin-coating process. To implement high-performance all-inkjet-printed OTFTs, highly conductive electrodes and gate dielectric layer with good insulating and surface roughness properties are required, which can be obtained from optimization of the ink formulation, inkjet-printing process and their thermal annealing conditions.

In this paper, we report all-inkjet-printed OTFTs with silver electrodes as gate and source/drain electrodes. Although soluble conductive polymers such as poly(ethylene dioxythiophene)/poly(styrene sulfonic acid) (PEDOT/PSS) and polyaniline (PANI) showed good performance for electrodes of OTFTs,^{5,11)} their high resistivity can limit application of polymeric conductors only to contact electrodes. Therefore, highly conductive metal ink such as silver ink is preferred in both contact and line electrode applications. By optimizing inkjet-printing and annealing conditions, we obtained reasonably good device perfor-

mance from OTFTs with silver electrodes, and organic dielectric layer.

2. Experimental Procedure

For all-inkjet-printed OTFTs fabrication, we used bare glass (Eagle 2000™) substrates cleaned by a standard solvent cleaning process (acetone, isopropylalcohol, and deionized water sequentially in an ultrasonic bath during 20 min, respectively) and it was dried at 200 °C in a convection oven for 30 min. For bottom gate electrode formation, a transparent metal–organic precursor type ink, INKTEC TEC-IJ-010, which has 15 wt % silver contents and viscosity from 9 to 15 cps, was inkjet-printed by using a piezoelectric (drop-on-demand) inkjet-printer (Dimatix DMP-2831). Substrate temperature was maintained at 60 °C during the inkjet-printing process to vaporize silver ink solvent quickly, resulting in better surface properties, film uniformity and shiny appearance. Inkjetting conditions were carefully optimized to obtain a highly conductive layer by controlling a waveform voltage, a cartridge temperature, an ink drop velocity and a fire frequency considering silver ink properties. The silver ink was printed with a drop velocity of about 5 m/s, and a drop spacing of 25 μm which means distance between ink drops. These two parameters determine thickness and width of the silver electrodes. Figure 1(a) shows capture images of ink droplet and drops that formed a well-defined electrode. After the gate electrode was printed, the substrate was annealed at 150 °C for 30 min in convection oven under atmospheric environment. We obtained a sheet resistance of $0.2 \Omega/\square$ from the 200 nm thick silver electrodes, which corresponds to specific resistance of $4 \mu\Omega\cdot\text{cm}$. On the fabricated silver gate electrode, poly(4-vinylphenol) (PVP) solution was inkjet-printed to form a gate dielectric layer. Cross-linked PVP is one of the most widely used organic insulation layer materials due to its good insulating performance and relatively low-temperature thermal curing condition. However, PVP solution jetting conditions should be optimized to obtain a well-defined gate dielectric layer because PVP solvent can easily result in cartridge nozzle clogging. PVP solution was composed of 10 wt % of PVP and 2 wt % of poly(melamine-co-formaldehyde) as a cross-linking agent (CLA) dissolved in propylene glycol methyl ether acetate (PGMEA) as a solvent. All chemicals were used as purchased from Sigma-Aldrich. PVP and CLA concentra-

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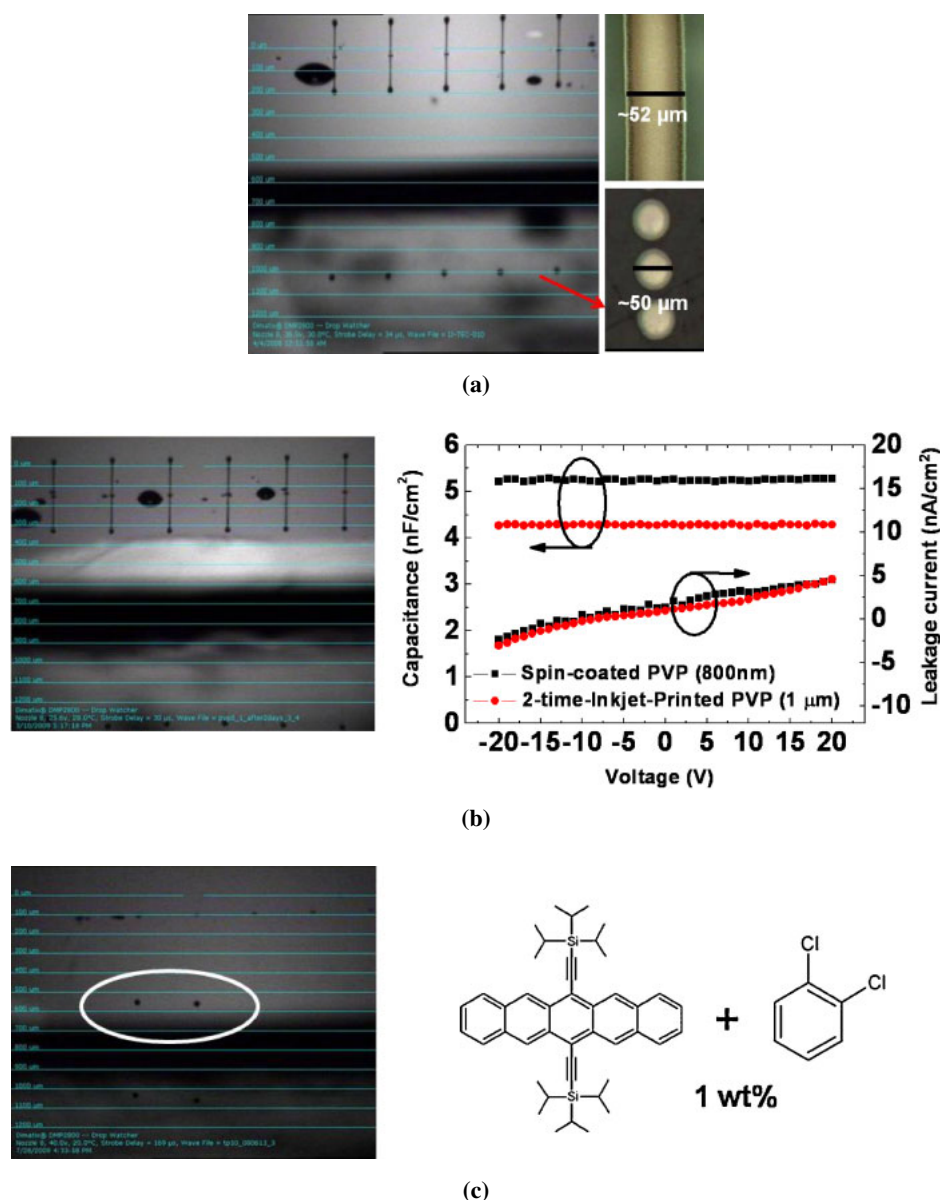


Fig. 1. (Color online) Optical capture images for (a) silver ink drop and silver line, (b) PVP solution drop and inkjet-printed PVP insulation performance comparing with that of spin-coated PVP layer, and (c) TIPS-pentacene drop from 10 μl cartridge with 21 μm diameter nozzles.

tions are critical factors to make a spherical shape of ink droplets which help forming a well-defined gate dielectric layer [Fig. 1(b)]. It is noted that relative composition of these two materials will determine viscosity of the PVP solution and insulation and surface energy property of the printed films.¹²⁾ PVP solution was inkjet-printed at room-temperature in order to prevent fast solvent evaporation which was found to degrade the quality of the printed film. Drop spacing of 25 μm was used for uniform dielectric film formation. To further improve surface and insulation property, we inkjet-printed two times producing 1 μm thick PVP layer. Since the PVP layer curing conditions are directly related to film quality and leakage current behavior, we optimized curing conditions for the 2-times-printing process, which will be reported elsewhere in detail.¹²⁾ Ramping up to 200 $^{\circ}\text{C}$ followed by 2-h soaking process was used, which produced a well-defined PVP gate dielectric layer with 4.3 nF/cm^2 and less than 0.5 nA/cm^2 at 0.2 MV/cm. The inkjet-printed PVP layer shows electrical

characteristics similar to the spin-coated PVP layer as shown in Fig. 1(b). Root-mean-square (RMS) values of surface roughness of the printed PVP layer were smaller than 4.1 nm for 10 μm by 10 μm scan area. After PVP dielectric layer was fabricated, silver source/drain electrodes were inkjet-printed by using the same conditions as those used for the gate electrode formation. Channel width (W) and length (L) of the fabricated OTFTs were 250 and 60 μm , respectively. Finally, 1 wt % of 6,13-bis(triisopropylsilyl)ethynyl pentacene (TIPS-pentacene) dissolved in 1,2-dichlorobenzene was inkjet-printed at room temperature to form $2 \times 2 \text{ mm}^2$ active layer. Figure 1(c) shows optical capture image of the TIPS-pentacene ink drops and molecular structure of TIPS-pentacene. It is noted that no surface treatment of the gate dielectric layer was used because PVP layer shows good interface characteristics with TIPS-pentacene.¹³⁾ TIPS-pentacene is one of most widely studied p-type organic semiconductor materials due to its high electrical performance and solubility in various organic solvent.^{1,3,14,15)} To

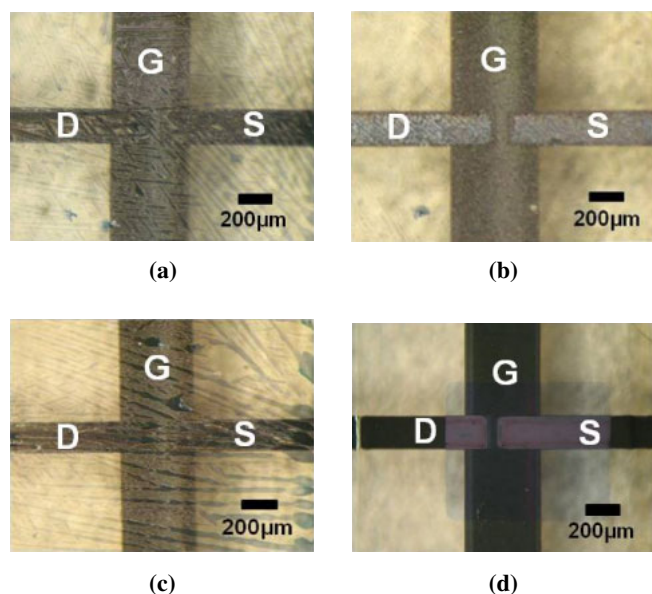


Fig. 2. (Color online) Optical microscope images for OTFTs with various TIPS-pentacene deposition methods including (a) inkjet-printing, (b) spin-coating, (c) drop-casting, and (d) reference evaporated pentacene on inkjet-printed TFT structure.

analyze the active layer formation method effect on OTFT electrical performances, TIPS-pentacene active layers were also formed at room temperature using spin-coating and drop-casting methods. In both cases, the active layers were not defined. After the TIPS-pentacene deposition, all films were dried in air at room temperature for an hour to maintain solvent rich environment during the solvent evaporation process. Thicknesses of the inkjet-printed, spin-coated, and drop-cast TIPS-pentacene layers were 280, 70, and 320 nm, respectively. Because 1,2-dichlorobenzene, which is an aromatic solvent, has a high-boiling-point, there will be enough time for molecules to self-assemble forming a highly ordered structure after the solvent was evaporated completely.^{6,15} We also fabricated OTFTs with the same structure, but with pentacene active semiconductor layer to compare interface properties between semiconductor and gate insulator layers. Pentacene was deposited using a thermal evaporator at 10^{-6} Torr on 60°C substrate, with a deposition rate of $0.3 \text{ \AA/s}$. The pentacene active area was defined by shadow mask as 1.5 mm by 1 mm and its thickness was 60 nm . Figure 2 shows optical microscope images of the fabricated OTFTs. It is noted that there are some structures in the inkjet-printed [Fig. 2(a)] and drop-cast [Fig. 2(c)] films in comparison with the spin-coated [Fig. 2(b)] one. We believe that spinning and drying during the spin-coating process can affect the crystalline structure formation, resulting in rather uniform and small crystalline structure for the spin-coating films. Details of the crystalline structure for the films will be discussed later. In all-inkjet-printing processes, inkjet-cartridge with $21 \mu\text{m}$ diameter nozzles and a capacity of 10 pl ink were used.

To measure the electrical properties of the OTFTs, current–voltage (I – V) characteristics of the fabricated OTFTs were measured in a dark box using Agilent 4155C semiconductor parameter analyzer. Thicknesses and surface profiles of metal and organic layers were measured using

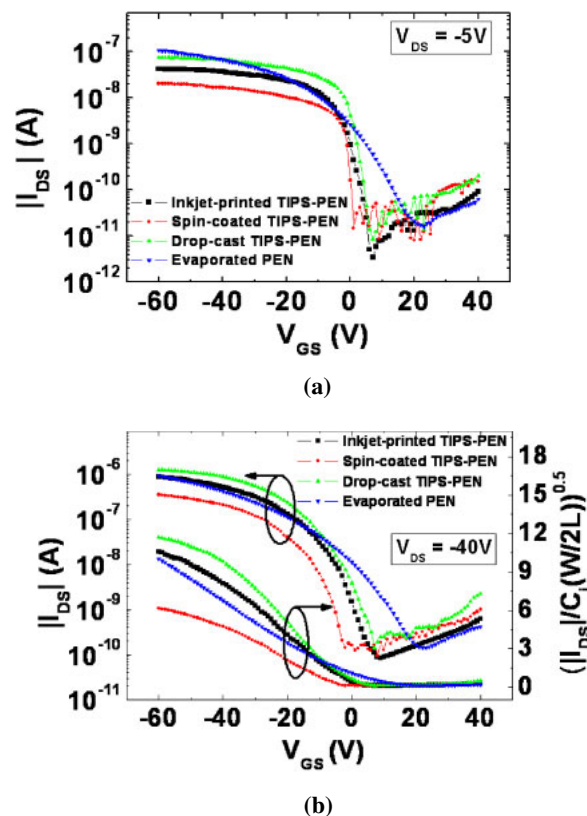


Fig. 3. (Color online) (a) OTFT transfer characteristic of (a) linear ($V_{\text{DS}} = -5$) and (b) saturation ($V_{\text{DS}} = -40 \text{ V}$) regimes.

both TENCOR Alpha-step 500 and atomic force microscopy (AFM) from Park System. X-ray diffraction (XRD) measurements of the pentacene and the TIPS-pentacene films were performed using a Mac Science powder diffractometer (M18XHF-SRA) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). All devices fabrication and measurements were executed in air-ambient.

3. Results and Discussion

Figure 3 shows the transfer characteristics of the fabricated OTFTs in (a) linear ($V_{\text{DS}} = -5 \text{ V}$) and (b) saturation regimes ($V_{\text{DS}} = -40 \text{ V}$). We obtained saturation mobility of 0.06 , 0.03 , and 0.09 , and $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, on/off ratio of 10^4 , 3×10^3 and 10^4 , and 10^4 , threshold voltage of -1.4 , -5.1 , and -2.8 , and 0.48 V for OTFTs with inkjet-printed, spin-coated and drop-cast TIPS-pentacene active semiconductor layers, and evaporated pentacene active semiconductor layer, respectively. It is also noted that, by using optimized inkjet-printing and annealing conditions, the electrical performances of the all-inkjet-printed OTFTs showed better performance than those of previously reported all-inkjet-printed OTFTs and are comparable to those of previously reported OTFTs with spin-coated PVP dielectric layer and/or thermally evaporated gold source/drain electrodes.^{16,17} This means that the inkjet-printed silver electrodes are suitable for the gate/source/drain and inkjet-printed PVP gate dielectric layer is well-matched with TIPS-pentacene active semiconductor layer.

It is noted that drain current of all solution-processed TIPS-pentacene OTFTs becomes saturated as V_{GS} increases

in negative direction while I_{DS} – V_{GS} characteristic of the pentacene OTFT shows linear behavior as shown in Fig. 3(b). This indicates that, for bottom-contact OTFTs with the inkjet-printed silver source/drain electrodes, TIPS-pentacene OTFTs show relatively poor contact resistance performance in comparison with the pentacene OTFT. Contact resistance can be analyzed by using a transmission line method (TLM) and we will report details of the contact resistance analysis of the solution-processed and evaporated OTFTs elsewhere.

Figure 3(a) shows that the TIPS-pentacene OTFTs have good switching performances with sub-threshold swing values of 3.17, 1.11, and 1.91 V/dec, for inkjet-printed, spin-coated, and drop-cast TIPS-pentacene OTFTs, respectively. These values are extracted between 10^{-11} and 10^{-9} drain current and are much smaller than that of the OTFT with the evaporated pentacene active layer (6.77 V/dec). As we mentioned, the surface energy of PVP dielectric layer is well-matched with that of TIPS-pentacene surface, making good interface properties than evaporated pentacene active semiconductor layer.¹³⁾ Using the defect density of insulator-semiconductor interface from amorphous silicon (a-Si) TFT model related to the sub-threshold as shown eq. (1),¹⁸⁾ we can extract $N_{SS}^{\max}$ values of 1.41×10^{12} , 4.75×10^{11} and 8.34×10^{11} , and $3.03 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ for OTFTs with inkjet-printed, spin-coated and drop-cast TIPS-pentacene, and evaporated pentacene active semiconductor layers, respectively.

$$N_{SS}^{\max} = \left(\frac{SS \log e}{kT/q} - 1 \right) \frac{C_{\text{ins}}}{q^2} \text{ (cm}^{-2} \text{ eV}^{-1}), \quad (1)$$

where SS , k , T , q , and C_{ins} represent the sub-threshold swing value (V/dec), the Boltzmann constant (eV K^{-1}), temperature (K), the absolute value of the electron charge (C), and the unit-area capacitance of the gate dielectric layer (F/cm^2), respectively. From these results, it is confirmed that the inkjet-printed PVP and TIPS-pentacene active semiconductor layers show similar defect density to that of the spin-coated PVP or SiO_2 gate dielectric layer and TIPS-pentacene active semiconductor layer.^{13,19)}

To further analyze crystalline structure affected by the active semiconductor layer deposition methods, we performed AFM and XRD measurements for all TIPS-pentacene and evaporated pentacene active semiconductor layers on the inkjet-printed PVP layer. The AFM images in Fig. 4 show that all the active semiconductor layers have crystalline structures even on the inkjet-printed PVP dielectric layer. TIPS-pentacene layers, unlike the pentacene layer, show longer c -axis structure although its size and shapes are different depending on the fabrication processes. Functional side groups of TIPS-pentacene attached to the central benzene ring of the pentacene molecule produce this orthorhombic crystal structure, and the molecular dimension along the side groups is larger than that along the pentacene molecule, resulting in a lower inter-planar spacing. It is known that this molecular structure renders TIPS-pentacene better stability for oxygen or water than the evaporated pentacene.²⁰⁾ In addition, formation of the large crystalline structure for the inkjet-printed and drop-cast TIPS-pentacene layers is confirmed. Slow solvent evaporation at room temperature produces highly ordered molecular structure and

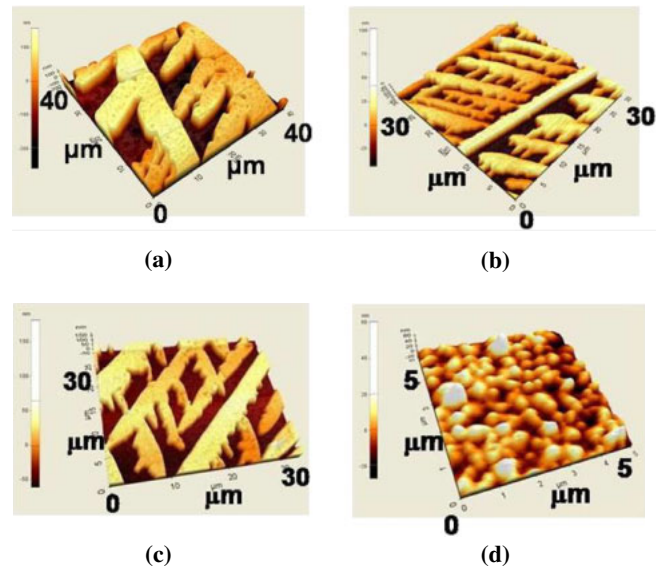


Fig. 4. (Color online) AFM images for active semiconductor layer on inkjet-printed PVP gate dielectric layer: (a) inkjet-printing, (b) spin-coating, (c) drop-casting, and (d) reference evaporated pentacene.

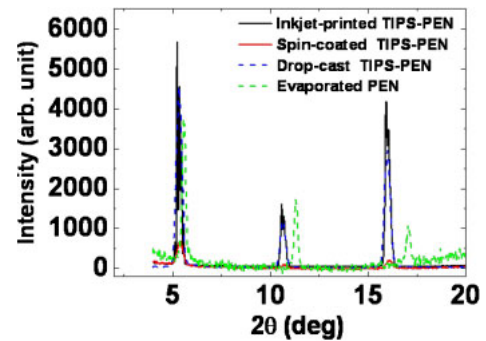


Fig. 5. (Color online) XRD spectra for inkjet-printed, spin-coated, drop-cast TIPS-pentacene, and reference evaporated pentacene on inkjet-printed PVP dielectric layer.

thus better electrical performance in comparison with the OTFTs with spin-coated TIPS-pentacene layer because spin-coating process have different effect on the TIPS-pentacene solvent evaporation.

Crystallinity of the TIPS-pentacene layers was estimated from the XRD measurement. Figure 5 shows XRD results for TIPS-pentacene and evaporated pentacene films on the inkjet-printed PVP layer. The evaporated pentacene and TIPS-pentacene films show peaks at 5.2, 10.5, and 15.9, and 5.6, 11.3, and 17.1° in 2θ values for $n = 1, 2$, and 3, respectively. From Bragg's law as shown in eq. (2), the XRD result for the pentacene active layer shows the (001) plane with an average interlayer spacing of 15.6 Å which is consistent with the previously reported results for pentacene films having orthorhombic structure.²¹⁾ For TIPS-pentacene active layers, there are same peaks at $2\theta = 5.2^\circ$ for the inkjet-printed, spin-coated and drop-cast films, which corresponds to an average layer separation of 16.8 Å. This value is also similar to that in a previous report and identical to that of the c -axis unit cell.^{3,13,14)}

$$2d \sin \theta = n\lambda, \quad (2)$$

where d , θ , n and λ are the interplanar distance, the scattering angle, an integer determined by the order given and the wavelength (here, λ is 1.54 Å), respectively. Although XRD patterns of the inkjet-printed, spin-coated and drop-cast TIPS-pentacene layers show peaks at the same theta values, inkjet-printed and drop-cast TIPS-pentacene showed much higher intensity which means their films had better and stronger molecular ordering than the spin-coated TIPS-pentacene film. It is closely related to the higher performance of OTFTs with the inkjet-printed and drop-cast films. In case of the spin-coated film, although active semiconductor layer film can be uniformly formed, solvent can be quickly evaporated in comparison with inkjet-printed or drop-cast films, leading to reduction in TIPS-pentacene crystallization time for the same high boiling point solvent used.

4. Conclusions

In conclusion, we successfully fabricated all-inkjet-printed OTFT with silver electrodes by using optimized inkjet-printing and annealing conditions of silver, PVP and TIPS-pentacene inks. The inkjet-printed OTFT showed low sub-threshold swing value indicating a good interface property between TIPS-pentacene and the inkjet-printed PVP dielectric layer. In addition, the inkjet-printed TIPS-pentacene layer showed similar crystallinity properties to the drop-cast TIPS-pentacene layer, resulting in better performance than OTFT with the spin-coated TIPS-pentacene layer. Therefore, well-optimized all-inkjet-printed OTFTs using inkjet-printed silver electrodes, PVP dielectric and TIPS-pentacene active layers can be used for low-cost, simply processed high-performance OTFTs and their circuit applications.

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- 1) S. K. Park, J. E. Anthony, and T. N. Jackson: *IEEE Electron Device Lett.* **28** (2007) 877.
- 2) J. Z. Wang, Z. H. Zheng, H. W. Li, W. T. S. Huck, and H. Sirringhaus: *Nat. Mater.* **3** (2004) 171.
- 3) S. K. Park, T. N. Jackson, J. E. Anthony, and D. A. Mourey: *Appl. Phys. Lett.* **91** (2007) 063514.
- 4) T. Kawase, S. Moriya, C. J. Newsome, and T. Shimoda: *Jpn. J. Appl. Phys.* **44** (2005) 3649.
- 5) H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, and E. P. Woo: *Science* **290** (2000) 2123.
- 6) S.-H. Lee, M.-H. Choi, S.-H. Han, D.-J. Choo, J. Jang, and S. K. Kwon: *Org. Electron.* **9** (2008) 721.
- 7) J. Doggart, Y. Wu, and S. Zhu: *Appl. Phys. Lett.* **94** (2009) 163503.
- 8) S. Gamerith, A. Klug, H. Scheiber, U. Scherf, E. Moderegger, and E. J. W. List: *Adv. Funct. Mater.* **17** (2007) 3111.
- 9) S.-H. Ko, H. Pan, C. P. Grigoropoulos, C. K. Luscombe, J. M. J. Fréchet, and D. Poulikakos: *Nanotechnology* **18** (2007) 345202.
- 10) D. Kim, S.-H. Lee, S. Jeong, and J. Moon: *Electrochem. Solid-State Lett.* **12** (2009) H195.
- 11) G. B. Blanchet, C. R. Fincher, and M. Lefenfeld: *Appl. Phys. Lett.* **84** (2004) 296.
- 12) S. Chung and Y. Hong: in preparation.
- 13) J. Kim, J. Jeong, H. D. Cho, C. Lee, S.-O. Kim, S. K. Kwon, and Y. Hong: *J. Phys. D* **42** (2009) 115107.
- 14) W. Lee, D. Kim, Y. Jang, J. Cho, M. Hwang, Y. Park, Y. Kim, J. Han, and K. Cho: *Appl. Phys. Lett.* **90** (2007) 132106.
- 15) C. S. Kim, S. Lee, E. D. Gomez, J. E. Anthony, and Y. L. Loo: *Appl. Phys. Lett.* **93** (2008) 103302.
- 16) Y.-H. Kim, Y. U. Lee, J.-I. Han, S.-M. Han, and M.-K. Han: *J. Electrochem. Soc.* **154** (2007) H995.
- 17) J. Kim, J. Cho, S. Chung, J. Kwak, C. Lee, Y. Hong, and J.-J. Kim: *J. Korean Phys. Soc.* **54** (2009) 518.
- 18) A. Rolland, J. Richard, J. P. Kleider, and D. Mencaraglia: *J. Electrochem. Soc.* **140** (1993) 3679.
- 19) S. H. Kim, D. Choi, D. S. Chung, C. Yang, J. Jang, C. E. Park, and S.-H. K. Park: *Appl. Phys. Lett.* **93** (2008) 113306.
- 20) S. K. Park, D. A. Mourey, J.-I. Han, J. E. Anthony, and T. N. Jackson: *Org. Electron.* **10** (2009) 486.
- 21) L. F. Drummy, P. K. Miska, D. Alberts, N. Lee, and D. C. Martin: *J. Phys. Chem. B* **110** (2006) 6066.