

# Ink-Jet-Printed Organic–Inorganic Hybrid Dielectrics for Organic Thin-Film Transistors

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Using a thermally crosslinkable organosiloxane-based organic–inorganic hybrid material, we formulated a functional ink suitable for ink-jet printing of dielectric thin films. Ink solvent chemistry plays an important role in producing a uniform dielectric layer. In particular, the hydrodynamic motion of the solvents is controlled during the drying period. We used a higher-boiling-point solvent in order both to prevent a nozzle from clogging and to suppress convective flow. We also incorporated a lower-boiling-point solvent of high surface tension for diminishing the outward Marangoni flow. We successfully applied the printed hybrid dielectric layer with smooth surface morphology to the gate dielectric layer for organic thin-film transistors and analyzed the electrical performance of the transistor based on the ink-jet-printed dielectric layer, comparing with that of the transistor based on the spin-coated dielectric layer.

## Introduction

Organic thin-film transistors (OTFTs) have received considerable attention recently because of their flexibility, low weight, low cost, and easy processability.<sup>1–4</sup> The performance of OTFTs has significantly improved in the past decade and has already reached a level comparable to that of hydrogenated amorphous silicon transistors.<sup>5</sup> However, relative to the impressive advances that have been made in OTFTs, little information has been reported on patterned gate dielectrics. Gate dielectrics should be patterned to access either the gate electrode in a bottom-gate configuration or the source/drain electrode in a top-gate configuration, so as to be applicable to active-matrix displays and integrated circuits.

Until now, the research for low-cost patterning processes of dielectric films has focused on photodefinable gate dielectrics such as polyvinylphenol, polyimide, acryl-based polymer, and sol–gel-derived siloxane-based hybrid polymer.<sup>6–13</sup> However, patterning photodefinable dielectrics should incorporate the photolithography technique, which is complicated and expensive since many process steps are required to construct one layer of a pattern. The ink-jet printing technique is an effective means of patterning a dielectric layer. A fully data-driven deposition of materials is accomplished simply in ink-jet printing by a one-step additive process of droplet-based liquids. However, detailed research on the ink-jet-printed dielectric layer has yet to be performed.<sup>14</sup> A major challenge in applying ink-jet techniques for the deposition of functional material is the formulation of suitable inks. Ink chemistry and formulations determine not only the drop ejection characteristics and stability but also the quality of the printed patterns.

In particular, the control of the spatial distribution of the solute during drying plays a vital role in producing a homogeneous and uniform ink-jet-printed dielectric layer. A significant

thickness variation would result in both capacitance fluctuation along the dielectric surface and a high leakage current through the thinner region of the dielectric layer. Therefore, nonuniform solute deposition (the so-called *coffee ring effect*), which is commonly observed in dried sessile droplets, should be prevented by controlling hydrodynamic motions of the solvent, that is, convective flow and Marangoni flow.

During evaporation of solvents incorporated in a printed droplet, while solvent molecules evaporated at the center of the droplet are readily reabsorbed, solvent molecules from the edge can easily escape without the reabsorbing process, which results in a larger evaporation rate around the edge.<sup>15</sup> Such a fast evaporation at the contact line induces an outward convective flow to compensate for the liquid removed by evaporation and, in turn, transports the suspending solute to the edge region.<sup>16</sup> At the same time, Marangoni flow can be involved in solute migration. Because the solvent evaporation requires the consumption of latent heat and because the thermal conduction path is longer at the top center of the droplet, the surface temperature is lower at the central region, which decreases the surface tension. This induces Marangoni flow from regions with low surface tension to regions with high surface tension (from edge to center).<sup>17</sup> However, in general, a single-solvent system, such as a temperature-gradient-driven Marangoni flow, is less dominant in the evaporating microdroplet than that in the convective flow. On the other hand, when using a mixture of low- and high-boiling-point liquids (dual solvent system), the solvent composition at the contact line will shift toward a higher fraction of high-boiling-point solvent than that in bulk due to the fast evaporation of the low-boiling-point solvent at the edge, which creates a compositional-gradient-driven Marangoni flow.<sup>18–20</sup> If a high-boiling-point solvent has a higher surface tension than that of a low-boiling-point solvent, an outward Marangoni flow is induced from the center to the edge. For the opposite case, in which a high-boiling-point solvent has a lower surface tension than that of a low-boiling-point solvent, an inward flow is

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induced. Therefore, for making a uniform layer without the coffee ring effect, both the direction and magnitude of each flow should be well-designed so as to either induce an inward flow or suppress an outward flow.

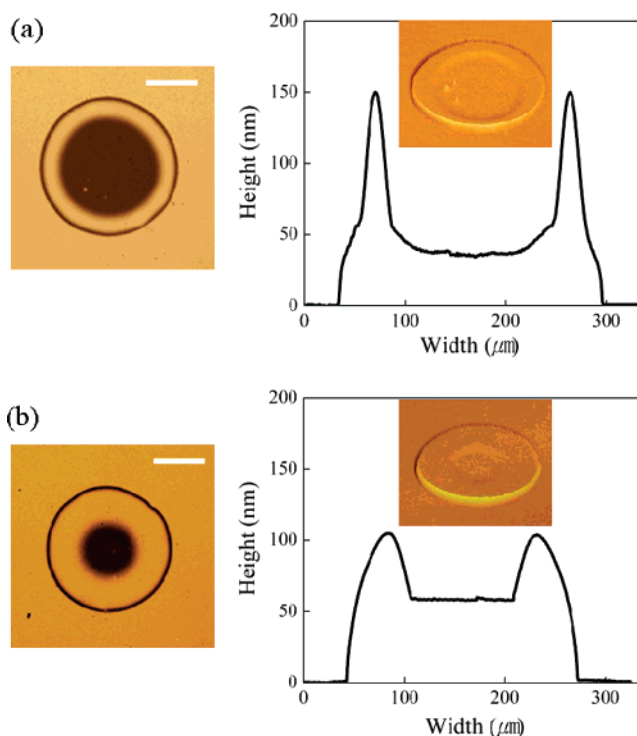
The present paper focuses on the ink solvent chemistry for ink-jet printing a dielectric layer with a smooth surface by controlling both convective and Marangoni flows. In addition, we fabricated an organic thin-film transistor using a printed dielectric layer and analyzed the electrical performance of the transistor, comparing with the transistor based on the spin-coated dielectric layer.

## Experimental Methods

A precursor solution for the organosiloxane-based organic–inorganic hybrid dielectric was synthesized by a sol–gel process using methyltriethoxysilane and tetraethylorthosilicate, and the details of the synthesis procedure can be found in our previous study.<sup>21</sup> Using a precursor solution, we fabricated both ink-jet-printed and spin-coated dielectric layers. For preparing the printable dielectric ink, various solvents were added to a hybrid dielectric precursor solution, while the precursor solution was diluted with ethyl lactate for spin-coating. Prior to film deposition, the formulated solutions were stirred to form homogeneous dispersions and then filtered through a membrane filter. A heavily doped silicon substrate was used as a substrate and cleaned by a wet method using trichloroethylene, acetone, isopropyl alcohol, methyl alcohol, and deionized water. The surface-native oxide on the Si substrate (a few angstroms thick) was not removed since its presence did not cause a variation in the electrical properties of the hybrid dielectrics. After the deposition process by spin-coating and ink-jet printing, the hybrid dielectric layers were heat-treated in air on a hot plate at 190 °C in order to evaporate the solvent and to complete the sol–gel reactions. The spin-coating was conducted for 25 s at 4000 rpm. The printer setup consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle (with an orifice size of 50  $\mu\text{m}$ ) manufactured by Microfab Technologies, Inc. (Plano, TX). The print head was mounted onto a computer-controlled three-axis gantry system exhibiting a movement accuracy of  $\pm 5 \mu\text{m}$ . The gap between the nozzle and the surface was maintained at about 0.5 mm during printing. Uniform droplet ejection was achieved by applying a 15  $\mu\text{s}$  long 35 V pulse at a frequency of 1000 Hz, and the printing procedures were performed onto the preheated substrate at 50 °C. The electrical properties of the hybrid dielectrics were investigated by capacitance–voltage ( $C$ – $V$ ) measurements at a frequency of 1 MHz and current–voltage ( $I$ – $V$ ) measurements using a Au/dielectric/heavily doped Si structure.

To fabricate a coplanar-type transistor, Au/Cr electrodes were patterned by a shadow mask on top of the printed hybrid dielectric on a heavily doped silicon substrate. The width and the length of the channel were 3 mm and 100  $\mu\text{m}$ , respectively. Next,  $\alpha,\omega$ -dihexylquaterthiophene (DH4T, Syncom B.V.) was deposited as an organic semiconductor between the source and drain electrodes by drop-casting a 0.8 wt % solution of DH4T in chlorobenzene.  $I$ – $V$  characteristics were measured in order to evaluate the electrical performance of the transistors. All  $I$ – $V$  and  $C$ – $V$  measurements were performed in air using an Agilent 5263A source-measure unit and an Agilent 4284A precision LCR meter, respectively. All samples were dehydrated in a vacuum atmosphere prior to the measurements.

The film thickness, two- and three-dimensional morphologies, the cross-sectional structure, and surface roughness were observed by a surface profiler (Dektak 150, Veeco Instruments



**Figure 1.** Confocal microscopic images and height profile as a function of dot width for the ink-jet-printed single dots obtained from the dielectric inks with varying solvent compositions of (a) EG/PrOH = 3:7 and (b) EG/MeEtOH/PrOH = 3:4:3 in a volume ratio. The scale bar in a two-dimensional confocal microscopic image is 100  $\mu\text{m}$ .

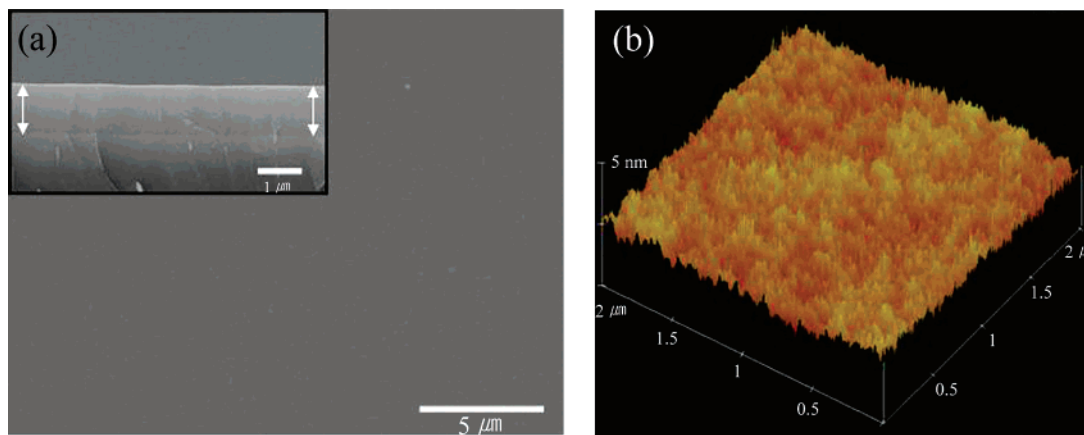
**TABLE 1: Fluid Properties of Solvents Used to Prepare Ink-Jettable Dielectric Ink**

solvent	viscosity (mPa·s)	surface tension (mN/m)	boiling point (°C)	vapor pressure (mmHg)
ethylene glycol	19.0	48.5	198	0.09
1-propanol	1.9	23.7	97	21
2-methoxyethanol	1.5	30.0	125	6.17

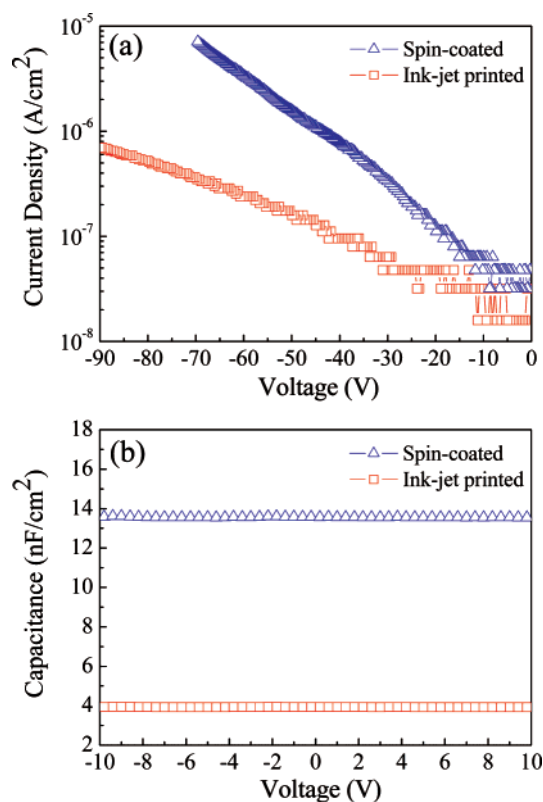
Inc.), laser scanning confocal microscopy (LEXT OLS3000, Olympus), scanning electron microscopy (JSM-6500F, JEOL), and atomic force microscopy (SPA 400, Seiko), respectively.

## Results and Discussion

For preparing the printable dielectric ink for ink-jet printing, the synthesized precursor solution was diluted, and 1-propanol (PrOH) was used as a dispersing medium for the sol–gel hybrid dielectric precursor. However, the ink based on a single solvent of PrOH tended to become clogged in a nozzle and prevented a uniform ejection of the droplets due to relatively rapid solvent evaporation. To obtain a stable jetting property, an appropriate high-boiling-point cosolvent (minor solvent) needs to be added in addition to the major solvent of PrOH. We selected ethylene glycol (EG) as a high-boiling-point cosolvent because EG is very miscible with both PrOH and the sol–gel hybrid dielectric precursor, and it can effectively inhibit premature drying at the orifice of the nozzle. The vapor pressure of EG is about 2 orders of magnitude smaller than that of PrOH, as shown in Table 1. It is also expected that the addition of EG into PrOH can assist in the production of a uniform solute deposition. PrOH preferentially evaporates at the contact line, and the local solvent composition shifts toward a higher fraction of the high-boiling-point solvent as the drying proceeds. In such a case, the evaporation at the contact line slows down, and the outward



**Figure 2.** (a) Scanning electron microscopy image and (b) atomic force microscopy image of the ink-jet-printed dielectric layer (plain view). The inset in (a) shows a cross-sectional view of the dielectric film.



**Figure 3.** (a) Current density–voltage and (b) capacitance–voltage characteristics of the ink-jet-printed and spin-coated gate dielectric layers. The film thickness of the spin-coated dielectric layer is 260 nm.

convective flow diminishes. Contrary to our expectation, however, the dot-shaped dielectric film printed from a single droplet of ink based on a mixed solvent of PrOH and EG exhibited a significant coffee ring effect, as shown in Figure 1a. Because the solid loading of the dielectric ink ( $\sim 1$  wt %) is much less than that of a typical conductive ink ( $> 20$  wt %), it would be more difficult to produce a uniform printed film from dilute dielectric ink.<sup>22–24</sup>

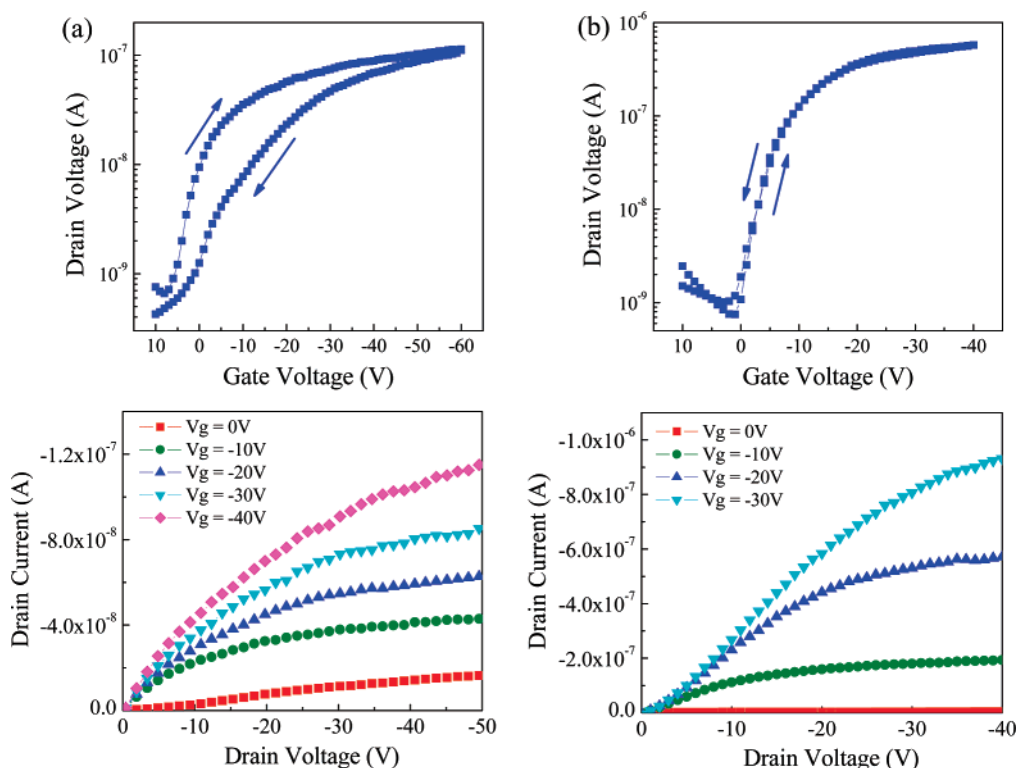
The high concentration of a high-boiling-point solvent at the edge of a droplet can also give rise to Marangoni flow because of the surface tension gradient. Because a high-boiling-point solvent (EG) has a higher surface tension than that of a low-boiling-point solvent (PrOH), the relatively fast evaporation of the low-boiling-point solvent around the contact line tends to increase the surface tension relative to the one in the center, which induces an outward Marangoni flow. Such a hydrody-

namic flow enhances the outward convective flow, by which the solute segregation around the contact line is maximized. The opposite case would be when a high-boiling-point solvent has a lower surface tension than that of a low-boiling-point solvent, in which case an inward Marangoni flow can develop in the evaporating droplet, which compensates the outward convective flow and, in turn, suppresses the coffee ring effect. However, we cannot find proper high-boiling-point solvents that have a lower surface tension than that of PrOH and are simultaneously miscible with the hybrid dielectric precursor solution.

To diminish the outward Marangoni flow, we substituted a part of PrOH with 2-methoxyethanol (2-MeEtOH). The magnitude of the Marangoni flow is determined by the Marangoni number  $M = \Delta\gamma L / \mu D$ , where  $\Delta\gamma$  denotes the surface tension difference between the center and the edge of the droplet,  $\mu$  is the viscosity of the mixed solvent,  $L$  is the length scale involved (i.e., the radius of the microdroplet placed on the substrate), and  $D$  is the diffusion coefficient.<sup>18,19</sup> The diffusion coefficient difference between various solvent systems can be negligible. Therefore, the surface tension difference and viscosity of the mixed solvent are important factors for determining the Marangoni flow magnitude. Table 1 compares the fluid properties of PrOH and 2-MeEtOH. The viscosities of these solvents are almost identical, whereas the surface tension of 2-MeEtOH is larger than that of PrOH. This means that the solvent substitution of 2-MeEtOH decreases the surface tension difference, thereby depressing the outward Marangoni flow and, in turn, minimizing the coffee ring effect, as shown in Figure 1b. The height ratio of the peak to valley for the dot-shaped dielectric film is 4.3 and 1.5 for PrOH-based and 2-MeEtOH-added ink, respectively.

Using hybrid dielectric ink with a composition of EG/2-MeEtOH/PrOH, we fabricated the ink-jet-printed hybrid dielectric layer by narrowing a dot-to-dot distance up to  $40\ \mu\text{m}$ . The surface of the printed dielectric film was flat and smooth, as shown in Figure 2. The film thickness and rms surface roughness of the ink-jet-printed dielectric layer were  $1.1\ \mu\text{m}$  and  $0.3\ \text{nm}$ , respectively. We observed no significant deviation ( $\pm 0.05\ \mu\text{m}$ ) in the film thickness over the printed area of  $1.0\ \text{cm}^2$ , excluding the  $200\ \mu\text{m}$  wide edge mounds. Although the coffee ring effect still exists in the single droplet film even after adding 2-MeEtOH, the uniform printed dielectric layer could be obtained by controlling the spacing between adjacent printed droplets. Therefore, it is believed that there is little influence of coffee ring effect on device performance such as a capacitance fluctuation along the dielectric surface, and a high leakage current through the thinner region of the dielectric layer.





**Figure 4.** Transfer and output characteristic of DH4T-based OTFTs fabricated using (a) ink-jet-printed and (b) spin-coated gate dielectric layers.

Figure 3a shows the current density–voltage characteristics of both the ink-jet-printed and the spin-coated hybrid dielectric. We observed that the ink-jet-printed hybrid film maintains a leakage current less than  $10^{-6}$  A/cm<sup>2</sup> until a bias of 90 V is applied. This indicates that the printed dielectric layer can withstand a stable transistor operation. However, taking the film thickness into consideration, the dielectric strength of the printed dielectric was  $\sim 0.8$  MV/cm (defined as an electric field at the current density of  $10^{-6}$  A/cm<sup>2</sup>), whereas the dielectric strength of the spin-coated hybrid film was 1.6 MV/cm. Such a difference could be attributed to the densities of the silanol groups present in the sol–gel-derived material. It is demonstrated that silanol groups act as trap sites for charge conduction through the dielectric layer, which results in a leakage current.<sup>21,25</sup> However, the condensation reaction consuming the silanol groups in the sol–gel material is a thermally activated process, and both dielectric layers are heat-treated at the same temperature of 190 °C. In this regard, they are believed to have the same number of the silanol groups, regardless of their processing method. Instead, we confirmed by an attenuated total reflectance Fourier transform infrared spectroscopy that EG remains in the ink-jet-printed dielectric layer. EG adsorbed on the dielectric was incompletely removed after heat treatment at 190 °C because of its high boiling point (198 °C). EG contains a hydroxyl group that acts as an electron trap for charge conduction by which the current can leak. In order to investigate the dielectric constant, we also analyzed the  $C$ – $V$  characteristic (Figure 3b), and the dielectric constant of the printed and spin-coated hybrid dielectric was found to be 4.9 and 3.9, respectively. The increased dielectric constant in the ink-jet-printed layer is also due to a higher concentration of the hydroxyl group with high polarity.

Figure 4 shows the transfer and output characteristics for OTFT fabricated using the ink-jet-printed and spin-coated dielectrics. The ink-jet-printed dielectric-based transistor shows a typical electrical behavior exhibiting a large hysteresis, while the spin-coated dielectric-based transistor represents little

hysteresis. In the previous study, it was demonstrated that the silanol group in the hybrid dielectric acts as a trap site for electrons injected from the gate electrode, which results in a hysteresis behavior. The hybrid dielectric heat-treated at 190 °C exhibits little hysteresis since silanol groups are annihilated by the condensation reaction at 190 °C.<sup>26</sup> However, the hydroxyl group incorporated in ink-jet-printed dielectric also acts as an additional trap site, which is responsible for the hysteresis behavior. It has been reported that the hydroxyl group in various organic dielectrics causes a gate charge-induced hysteresis as well as slow polarization-induced hysteresis due to sluggish orientation of the dipoles.<sup>25,27,28</sup> In order to compare the electrical performance of both transistors, we calculated the electrical performance parameter. The off-current, field-effect mobility, and threshold voltage calculated from the off-to-on characteristic of the ink-jet-printed dielectric-based transistor are  $6 \times 10^{-10}$  A,  $2 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and 8 V, respectively. In the case of the spin-coated dielectric-based transistor, the off-current, field-effect mobility, and threshold voltage are  $6 \times 10^{-10}$  A,  $5 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and  $-0.3$  V, respectively. Both transistors based on the printed and the spin-coated dielectrics had almost identical field-effect mobility and off-current values, indicating that the ink-jet-printed dielectric film is electrically comparable to the spin-coated one. However, it is observed that the threshold voltage for the printed dielectric-based transistor was significantly shifted toward a positive voltage. This threshold voltage shift resulted from the existence of the hydroxyl group in EG contained in the printed dielectric layer. It is well-known that hydroxyl groups can be negatively charged by capturing the electrons in the conventional SiO<sub>2</sub>-based dielectric in a Si MOSFET.<sup>29</sup> The presence of negative traps within the dielectric layer would facilitate accumulation of holes at the interface between the gate dielectric and the semiconductor, inducing a positive shift in the threshold voltage. This implies that dielectric ink formulation should be well-designed in terms of not only the ink jetability and deposition uniformity but also the electrical performance.

## Conclusions

We have developed ink-jet-printable dielectric inks based on organic–inorganic hybrid sol–gel materials. The ink composition was carefully controlled to ensure a stable jetting behavior and to reduce a nonuniform deposition after the solvent dried. The ink-jet-printed dielectric films exhibited smooth surfaces with the rms surface roughness of 0.3 nm. It was observed that the leakage current through the printed dielectric is less than  $10^{-6}$  A/cm<sup>2</sup> until a bias of 90 V is applied, and the dielectric constant of printed dielectric is 4.9. In addition, it was confirmed that the ink-jet-printed dielectric layer performs electrically similarly to their spin-coated counterparts. However, the residual solvent molecules induced a large hysteresis behavior and positive shift of the threshold voltage for the printed dielectric-based organic transistor.

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