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Fluorosurfactant-assisted photolithography for patterning of perfluoropolymers and solution-processed organic semiconductors for printed displays

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A photolithographic patterning technique of perfluoropolymers was developed for the micropatterning of solution-processed organic semiconductors. We found that a small amount of fluorosurfactant additives in photoresist solutions enabled preparation of the spin-coated films even on the dewetting surfaces of perfluoropolymers. Subsequent photolithography and dry/wet etching achieved excellent patterning of perfluoropolymers, which provided a high contrast of wettability in microscale on the substrate. The dewetting patterns were applied for isolating solution-processed organic thin-film transistor arrays for a 100 ppi active-matrix display by selective dewetting. The isolation of the semiconducting layers achieved significant improvement in the current on/off ratio with a high mobility of $>1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

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The recent achievements of high mobility in solution-processed organic field-effect transistors (OFETs) have led to a consideration of printed manufacturing of practical electronic devices, such as active-matrix organic light-emitting diode (AMOLED) displays and radio-frequency identification tags.^{1–3} In order to achieve printed manufacturing, the development of surrounding materials and technologies such as solution-processable gate dielectric materials,^{4,5} high-resolution patterning techniques of solution-processed organic semiconductors,^{6–11} and water/gas barrier films^{12,13} has become of great importance. Perfluoropolymers are promising materials for those purposes because of their unique physical and chemical properties, which include a low dielectric constant and low index of reflection, their inherently clean and non-stick hydrophobic nature, and high chemical stability and gas-barrier properties. Among the perfluoropolymers, the amorphous soluble perfluoropolymers Cytop (Asahi Glass) and Teflon AF (DuPont) [Fig. 1(a)], have been used in OFETs owing to their low- k ($\epsilon = 2.1$) properties that reduce dipolar disorder at organic/dielectric interfaces and very high breakdown electric field of $\sim 5 \text{ MV cm}^{-1}$.^{14–17} Cytop is also useful for a solution-processed protective barrier layer for organic semiconductor devices from the oxygen and water in air.^{18,19} However, in spite of these remarkable characteristics, the use of perfluoropolymers has been limited because of the difficulty in patterning them, which is because of an incompatibility with conventional photolithography techniques. Perfluoropolymers' surfaces have extremely weak interactions with most of molecules, and hence, the deposition of photoresist films by spin coating is prohibited.

Since the unique properties of the perfluoropolymers offer versatile applications in a variety of research fields, there has been a tremendous need for developing patterning techniques not only in the field of electronics,^{20,21} but also in micro/nano fluidics and cell biology,^{22,23} therefore, several techniques have been proposed thus far. For example, a weak oxygen plasma etching modifies the surface of Teflon AF to have O–C–O and C=O species that enable photoresist to be spin coated.²⁰ Similarly, 1-nm-thick vacuum-evaporated Al that transformed into an AlO_x layer by air exposure is able to modify the Cytop surface such that it can be wetted for photoresists.²¹ The photolithography and lift-off technique of perfluoropolymers were developed for the patterning

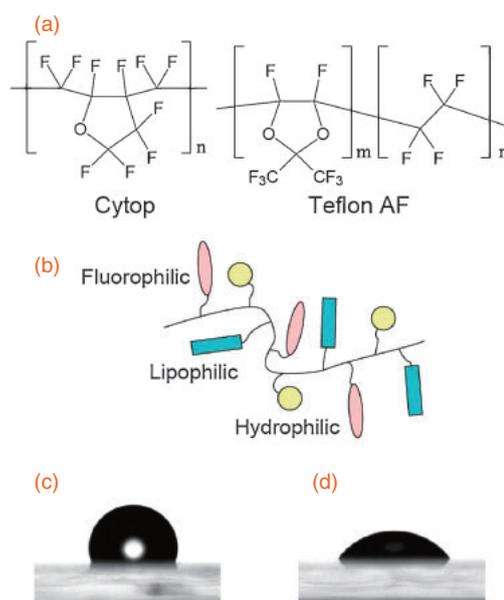


Fig. 1. Chemical structures of Cytop and Teflon AF (a) and schematic of polymeric fluorosurfactant having fluorophilic, lipophilic, and hydrophilic groups (b). Contact angles of pure water (c) and water with 0.02 wt% of S-386 additive (d).

of organic semiconductors or living cells.^{22,23} However, the surface modifications lead to contaminations, which spoil the inherently clean nature of perfluoropolymers, while the lift-off of such polymers has a difficulty in the obtainment of sharp edges. Therefore, it is still desirable to develop simple and high-resolution patterning techniques of perfluoropolymers.

In the present study, we have established a very simple technique that enables photoresist to be spin coated on the surface of perfluoropolymers without modifying their clean surfaces. The key material is a fluorosurfactant of which a small amount of 1 wt% was added into commercially available common photoresists. This allowed the wetting of the photoresist solution on the surfaces of both Cytop and Teflon AF. The use of fluorosurfactant additives in photoresist was considered by Cho et al.²⁰ previously; in this work, fluorosurfactants, however, did not work efficiently, thus requiring unusual spin-coating techniques, i.e., spin coat twice with heated substrates using a high-fluorosurfactant concentration

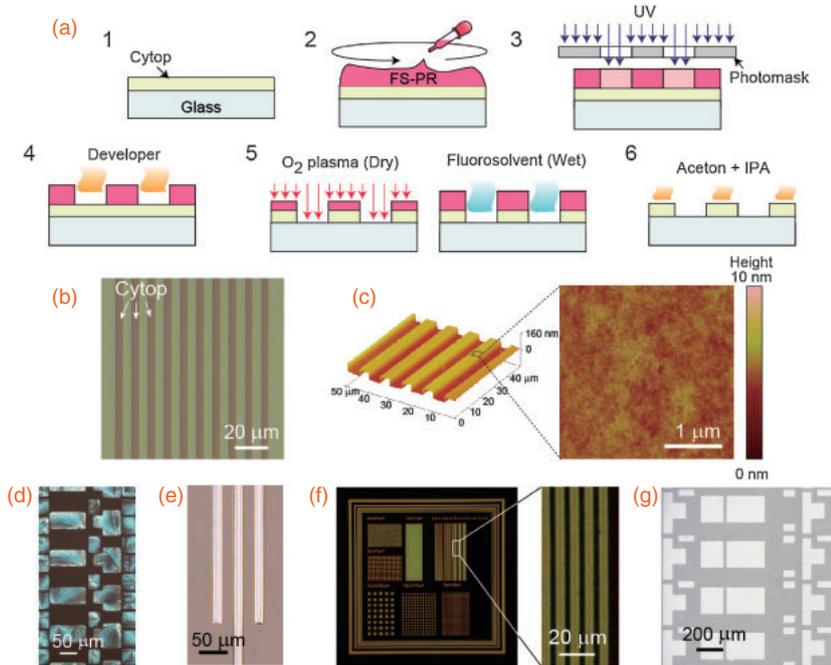


Fig. 2. (a) Schematic of the patterning process flow. On top of Cytop layer on glass substrate (1), the fluorosurfactant-added photoresist (FS-PR) layer was prepared by spin coating (2). Subsequent UV exposure (3), development (4), O₂ plasma or fluorosolvent etching (5) achieved patterning of Cytop, and rinsing with acetone and isopropyl alcohol (IPA) removed residual FS-PR layer (6). Optical micrograph (b) of Cytop stripes with 5- μm ridge with 5- μm spacing and AFM images (c) of corresponding area. The AFM image on the right was obtained from the surface of the remaining Cytop. Solution-processed TIPS-pentacene film (d) and silver electrodes (e) patterned by selective-dewetting using patterned Cytop. TIPS-pentacene solution and silver ink remained only in the etched area and formed continuous film. (f) Photoluminescent image of a light-emitting polymer patterned by dry etching technique. (g) Optical micrograph of patterned Cytop by using wet etching technique [5 in (a)]. The white rectangles, where were etched by fluorosolvent, were designed to define the area of semiconductors, through holes and OLEDs in AMOLED display.

of 15 wt%, which lowered the performance of the photoresist. In contrast, in our study, the 1 wt% of fluorosurfactant additives did not sacrifice the processability and the performance of the original photoresists; hence, high-resolution patterning was achieved. By using the patterned perfluoropolymer as a repellent bank, we successfully achieved excellent patterning of thousands of OFETs in a backplane circuit of a 100 ppi AMOLED display by a simple solution process. The patterned OFETs showed significant improvement in current on/off ratio and subthreshold swing as well as reasonably high mobility.

To enable spin coating of photoresists on bare perfluoropolymer surfaces, we modified photoresist solutions by a fluorosurfactant Surflon S-386 (AGC Seimi Chemical), which is a non-ionic, polymeric surfactant with fluorophilic, lipophilic, and hydrophilic groups in its structure [Fig. 1(b)]. These features enable Surflon S-386 to dissolve in water as well as common organic solvents and contribute to the preparation of wetting droplets on the bare Cytop surfaces. In fact, we found 0.02 wt% of Surflon S-386 additive decreased the water contact angle on Cytop drastically from 110 to 55° as is shown in Figs. 1(c) and 1(d). We tested the compatibilities of Surflon S-386 with two types of photoresists, which are S1813G (Rohm and Haas) for the positive type and ZPN-1150 (Zeon) for the negative type, and we found a 1 wt% additive into the photoresist solutions enabled spin-coated films on Cytop and Teflon AF surfaces. Full coverage was obtained even with a relatively large size, i.e., 10 cm square substrate. The rest of the photolithography process was carried out without re-optimization of our recipe. We note that in the following experiments we will show the results obtained with Cytop, but all the techniques developed herein are also applicable to Teflon AF.

After the patterning of the photoresist layer by ultraviolet (UV) exposure and development, the Cytop underneath the patterned photoresist layer was patterned by either oxygen plasma or wet etching, using the photoresist layer as a mask [Fig. 2(a)]. The oxygen plasma etching (200 W for 6 min)

enabled us to prepare a high-resolution patterning with features of 5 μm [Fig. 2(b)]. The edge of the patterned Cytop was confirmed to be very abrupt by an atomic force microscope (AFM) measurement [Fig. 2(c)]. Additionally, the surface of the patterned Cytop was very smooth without any adsorbed substances with a root mean square roughness (RMS) of 0.40 nm, which is the same as the as-deposited Cytop layer. This indicates the fluorosurfactant molecules were rinsed off perfectly and did not remain; therefore, the surface maintained the inherently clean nature of Cytop even after the photolithography and etching processes. This is also confirmed by the contact angle measurement, which revealed both the patterned Cytop and the as-deposited one showed the same water contact angles of 110°. Meanwhile, oxygen plasma etched regions became highly wetted, demonstrating the high contrast of wettability between the remaining Cytop and the etched regions. This enables various kinds of solution-processed functional materials, such as soluble organic semiconductors and silver-nano inks, to be patterned by selective dewetting [Figs. 2(d) and 2(e)].

The combination of fluorosurfactant-assisted photolithography and oxygen plasma etching also enabled high-resolution patterning of organic semiconductor films. To demonstrate this, we inserted a light-emitting polymer [Super yellow (Merck)] layer in between the substrate and Cytop layer and carried out the same process in Fig. 2(a). The light-emitting polymer layer was etched by oxygen plasma along with the Cytop layer and the resolution achieved, limited by our photolithography process, was $\sim 3 \mu\text{m}$ [Fig. 2(f)]. This technique is similar to the previously reported method by Chang et al.²¹⁾ but it is simpler in that our process does not require a vacuum-evaporation process for preparing an ultrathin adhesive layer. A wet-etching technique has also been developed using a fluorosolvent of FC-43 (3M) as an etchant for Cytop [5 in Fig. 2(a)]. Although the resolution achieved was not as high as with the oxygen plasma etching process, we achieved feature sizes of several tens of micrometers [Fig. 2(g)], which is enough that they can be

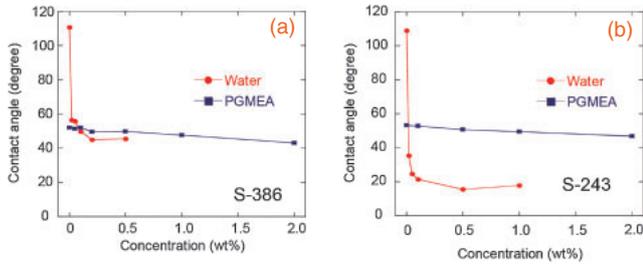


Fig. 3. Contact angles of water and PGMEA solutions on Cytop surface as a function of concentration of polymeric fluorosurfactant of Surfion S-386 (a) and of monomeric fluorosurfactant of Surfion S-243 (b).

used as repellent bank structures for display applications. We would like to stress that the advantages of the wet etching over the oxygen plasma etching are not only the ease of processing but also the high process compatibility with plastic substrates, of which the surfaces are damaged seriously if they are exposed to oxygen plasma.

In order to understand how the fluorosurfactant additives enabled adhesion of photoresist on Cytop, we conducted detailed contact angle measurements with Surfion S-386 for water and propylene glycol methyl ether acetate (PGMEA), which is a solvent for the photoresists, as well as with a monomeric fluorosurfactant Surfion S-243 that was not used to facilitate spin coating of photoresist solutions on Cytop (Fig. 3). In the case of water, 0.1 wt% additives of either Surfion S-386 or S-243 decreased the contact angles dramatically to 50 and 21°, respectively, and further addition of fluorosurfactants did not change the angle remarkably. This indicates S-243 was more effective than S-386 for lowering the surface tension of water. In contrast, the effects on PGMEA were small for both the fluorosurfactants. The contact angle of pure PGMEA was 52°, and that decreased gradually to 43 and 45° for S-386 and S-243, respectively, even with a relatively high concentration of 2 wt%. These results imply the decrease of the surface tension of photoresist solutions is not a main mechanism that enabled photoresist films to be spin coated on Cytop. Although the effect of Surfion S-243 additives was more effective for reducing contact angles, S-243 did not contribute to the spin coating of the photoresist solution. The small change of the wettability on the PGMEA solution also suggests the mechanism is not related to the surface tension of the solutions. It would be interesting if we could explain the differences of the fluorosurfactants based on their chemical structures; however, this is impossible since their chemical structures are not disclosed. Nevertheless, the apparent difference between those two fluorosurfactants is their molecular sizes, i.e., Surfion S-386 is a polymeric surfactant while S-243 is monomeric. We therefore used the other fluorosurfactants to understand the difference between the polymeric and the monomeric fluorosurfactants empirically. For the other polymeric fluorosurfactants, we tested Surfion S-651 and Novec FC-4432 (3M) and found they also enabled the spin coating of photoresist solutions on Cytop with additive concentration of less than 1 wt%. In contrast, we were not able to obtain any spin-coated films with the monomeric fluorosurfactants Surfion S-420 and Zonyl-FSO (DuPont). These results suggest that the complicated adsorbed structures of the polymeric surfactants with a number of anchoring substituents is

important to interact more effectively with substrates than a simple self-assembled monolayer (SAM) of monomeric surfactants.²⁴⁾

Since our patterning technique of Cytop is able to provide high resolution with very high contrast of wettability, it enables us to prepare high resolution repellent banks that are strongly required for the fabrication of high-resolution printed displays.²⁵⁾ We demonstrated a bottom-gate, bottom-contact OFET array for a 100 ppi AMOLED display based on a small molecule-based p-type organic semiconductor Lisicon S1200 series (Merck). After the patterning of gold source and drain contacts on a 300-nm-thick photocurable polymeric dielectric, the semiconductor area was defined by 60 nm of Cytop bank, which was further defined by the fluorosurfactant-assisted photolithography with a negative photoresist of ZPN-1150 modified with 1 wt% Surfion S-386. The semiconducting layer was deposited and patterned by selective dewetting, which achieved an excellent isolation of the active regions as shown in Fig. 4(a). We note that 60-nm-thick Cytop is relatively thin for the bank structure; however, the semiconductor solution remains only in the patterned area by the surface tension of the solution, and thus a well-separated semiconducting layer was obtained.

The transfer characteristics in Fig. 4(b) show that the patterning of the semiconductor resulted in significant improvement in the current on/off ratio. The unpatterned device, of which the film was prepared by standard spin coating, showed a high mobility of $1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ but a low on/off ratio of 10^2 due to the high off current. In contrast, the off current decreased dramatically in the patterned device; thus, a very high on/off ratio exceeding 10^7 and a sub-threshold swing of 0.42 V/dec were achieved. The off current of the order of 10^{-12} A was on the same order as the gate leakage current, indicating the off-channel current was fully suppressed. The highest mobility among the 25 devices was $1.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is almost the same as that for the unpatterned device, and the average mobility obtained was $0.65 \pm 0.31 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The relatively large variation of mobility is probably related to the differences in the size and orientation of the crystals in each device. To obtain better device uniformity, a high mobility semiconducting polymer poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-*b*]thiophene) (PBTTT-C16) was also evaluated in the patterned array with an octadecyltrichlorosilane (OTS)-treated SiO_2 dielectric [Fig. 4(c)]. It should be noted that hydrophobic SAMs, such as OTS, were typically used for defining dewetting regions where semiconductors should not be deposited;^{3,8,9)} however, Cytop is more hydrophobic and thus PBTTT-C16 films were formed selectively on the OTS-treated region. Twenty driving transistors were tested and all the devices showed typical p-channel FET characteristics with a threshold voltage of $4.2 \pm 1.5 \text{ V}$ and an average mobility of $0.12 \pm 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Although the average mobility is slightly lower than that of Lisicon S1200, the device uniformity was successfully improved, probably due to the small crystal domain size ($\sim 200 \text{ nm}$) that minimized the effect of the differences in molecular orientation and averaged the device performance.

In summary, we have developed a simple and versatile photolithography technique that enables high-resolution patterning of perfluoropolymers. This is achieved by modify-

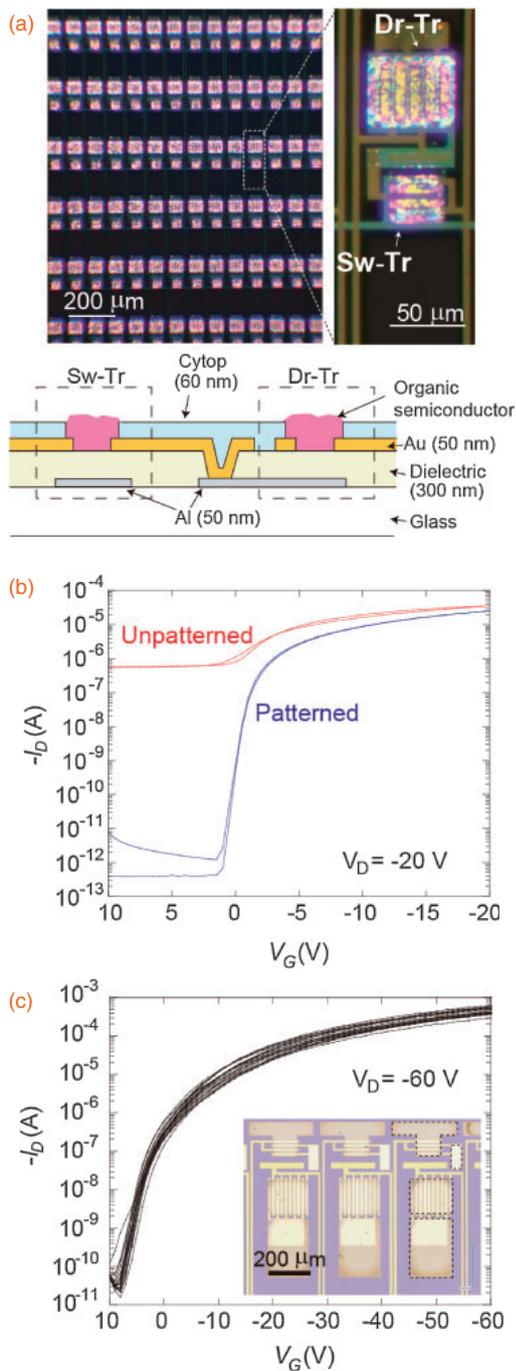


Fig. 4. (a) Polarized optical micrograph of solution-processed transistor array for 100 ppi display. The solution-processed organic semiconductor of Lisicon S1200 was patterned by selective dewetting by Cytop bank. The sizes of the patterned semiconducting area of driving transistor (Dr-Tr) and switching transistor (Sw-Tr) are 50×40 and $28 \times 29 \mu\text{m}^2$, respectively. The bottom figure shows cross-sectional schematic view. (b) Comparison of transfer characteristics at $V_D = -20$ V of the patterned and unpatterned Dr-Tr. The channel length and width of Dr-Tr are 5 and 160 μm , respectively. (c) Transfer characteristics of twenty of PBTTC-16-based Dr-Tr for 25 ppi display. The channel length and the width are 10 and 1530 μm , respectively. The inset shows the optical micrograph of the PBTTC-16-based transistor array for 25 ppi display. The rectangles drawn by the dashed lines are the area of the patterned PBTTC-16 film.

ing commercially available photoresists by adding a small amount of the non-ionic polymeric fluorosurfactant Surfion S-386, S-651, or Novec FC-4432. These additives enabled

spin coating of photoresist on the Cytop layer without modifying its fluorinated hydrophobic surface. Since the patterned Cytop enables pattern wetting and dewetting regions, functional inks such as organic semiconductor solutions and silver-nano inks were used for patterning by selective dewetting on a microscale. We used this technique for fabricating a solution-processed organic backplane circuit for a 100 ppi AMOLED display. The patterning of the organic active layer improved the on/off ratio dramatically from 10^2 to 10^7 and resulted in sufficiently high mobility. We think patterning of surface wettability is crucially important in printed electronics for achieving higher resolution with ease of fabrication. The developed techniques are able to contribute significantly to this purpose.

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