High Resolution Patterning of Functional Inks using Wettability and Repellency Control Method and Its Application to Electronic Devices

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High performance and easily processable wettable/repellent patterns formation were achieved using photo-induced surface control materials (PISC) by conventional i-line exposure and annealing. Functional inks can be patterned spontaneously on exposed surface which realize high resolution patterning by drop-coating methods. Fine silver lines of 10-μm width were achieved by inkjet printing with Ag nanoparticle (AgNP) inks on this pattern. Using this technique, silver source-drain electrodes of organic thin film transistor (OTFT) were successfully fabricated. A novel patterning method using alkali-developable type PISC was also devised for formation of high resolution, aspect patterns and high thickness microlenses, which difficult to be formed by photolithography technique.

Keywords: Wettability repellency Control, Self-patterning, High resolution patterning, High aspect patterning, Printing, Photolithography, Microlens

1. Introduction

Printing technology has attracted attention because of low cost, reduction of environmental load and compatibility with fabrication of a large variety of electronic devices, such as wearable and flexible devices. However, high resolution direct printing of functional inks required for industrially available electronic devices is difficult due to spreading and bleeding of the printed solution patterns. Accordingly, some groups have suggested new printing techniques using surface wettability control method to form fine patterns or the fabrication methods of controlled surface. For example, lyophilic photoresist patterning by solvent etching [1], oxygen plasma treatment of functional polymer films through shadow mask [2,3], degradation of photo-sensitive self-assemble monolayer (SAM) by ultraviolet (UV) exposure [4-6], and surface activation of an amorphous perfluorinated polymer layer by irradiation of vacuum UV light [7] were proposed. These works have been given predefined hydrophilic/hydrophobic patterned surface and the spreading and bleeding of printed pattern are suppressed on these guide patterns because the patterned hydrophilic area should primarily be wetted by the inks. Furthermore, if enough contrast of contact angle of inks between on hydrophilic and hydrophobic area exists, ink droplets are patterned only on the hydrophilic area spontaneously [8,9], that is to say, self-patterning on wettable area (Fig. 1).

To utilize this method for mass production process, much simpler and higher throughput method of forming wettable/repellent patterned surface is needed. Recently we are developing photo-induced surface control material (PISC) which can form hydrophilic/hydrophobic pattern using mild UV...
exposure and annealing and provide very high wettable/repellent contrast patterns. The PISC films coated on substrates shows high liquid repellency toward hydrophobic solvents or aqueous solutions and dispersions. Following mask UV exposure of i-line and annealing convert repellent surface to wettable patterns with the partial degradation of hydrophobic polymer in PISC. In this study, we show two types of PISCs, i) UV curable type on exposure area (PISC1) and ii) alkali-soluble positive tone resist type (PISC2). Both PISCs can assist self-patterning of functional inks (Fig. 2). We report patterning results of Ag nanoparticle (AgNP) inks using PISC 1 and its application to fabrication of organic thin film transistor (OTFT). We also devise novel patterning methods of UV curable inks for the formation of high aspect and resolution patterns or microlenses by PISC2.

2. Experimental

The Photo-induced surface control material, UV curable type PISC-X200, alkali-developable type PISC-X007 and PISC-X007H were prepared in JSR Corporation. AgNP ink NPS-JL was obtained from Harima Chemicals Inc. and Drycure Ag-JB 1020B was obtained from C-INK Co., Ltd. UV curable inks were also prepared for the formation of high aspect and resolution patterns or microlenses by PISC2. Black pigment-dispersed UV ink UV-IJ Black (T&K TOKA Co., Ltd.) was used as received. White pigment-dispersed ink was prepared by mixing of dispersion of titanium dioxide (TiO₂) in tetradeacane and typical epoxide monomers and photo acid generators. UV curable ink for microlens formation was prepared by mixing of acrylate monomers, oligomers and photo radical initiators.

Patterns of PISC-X200 were prepared on glass substrate (Eagle XG, Corning) by spin coating. The sample films were dried on a hot plate at 90 °C for 2 min. The thickness of films was about 0.5 μm. UV irradiation was performed in air using a mask aligner with ghi line mixture (MA-1400, Japan Science Engineering Co., Ltd.). The intensity of the light was measured with UIT-250 (Ushio Inc.). Chrome masks (Mitani Micronics Co., Ltd.) were used for PISC patterning by contact exposure. After UV exposure, the sample films on substrate were annealed on a hot plate at 70 °C for 15 min.

Patterns of PISC-X007 were prepared in the same manner. The thickness of films was from 0.5 μm to 10 μm according to the target patterns. High viscosity type PISC-X007H was used for the formation of high thickness pattern over 5 μm. After mask UV exposure and annealing, resulting films were dipped into 2.38 wt% tetramethylammonium hydroxide (TMAH) solution for 120 sec. as development and pure water for 60 sec as rinse. The resulting substrates were dried on hot plate at 90 °C for 5 min.

The thickness of the films was measured by Surface Profilometer (KLA-Tencor, Alpha-Step IQ). Contact Angle of films was measured by contact angle meter (Kyowa Interface Science Co., Ltd., DM-501Hi or MCA-2). Functional inks were drop-coated by Inkjet printer (Fujifilm Dimatix, DMP-2831) or microcapillary (Kyowa Interface Science Co., Ltd., MCA-2). Resulting patterns were observed using microscope (Nikon Instec Co., Ltd., ECLIPSE L200) or Scanning Electron Microscope (Hitachi High-Tech Corporation, Regulus 8100).

3. Results and discussion

3.1. Formation of hydrophilic/hydrophobic patterns

The surface wettabilities on PISC-X200 coated substrates were evaluated using water and tetradeacane contact angle measurement. The
variations in contact angle as a function of UV dose are shown in Fig. 3a. Drastic decrease of both water and tetradecane contact angle was observed around 50 mJ/cm² exposure and the contact angle was saturated after that. Thus, PISC can produce low energy and high throughput process, while most of surface wettability control techniques need high energy, short wavelength light exposure.

Figure 3b shows tetradecane droplets behavior on repellent area and 50-μm width of wettable area. Variations in contact angle as a function of UV dose are shown in Fig. 3a. Drastic decrease of both water and tetradecane contact angle was observed around 50 mJ/cm² exposure and the contact angle was saturated after that. Thus, PISC can produce low energy and high throughput process, while most of surface wettability control techniques need high energy, short wavelength light exposure.

Figure 3b shows tetradecane droplets behavior on repellent and wettable area patterned by 200 mJ/cm² UV exposure through a 50-μm width of line patterns mask. Due to the huge difference of contact angle between exposed and unexposed area, tetradecane droplets spread only on 50-μm width exposed area without any overspill. We found that the film thickness reduction on wettable area because of the chemical degradation and curing shrinkage of polymer including in PISC-X200 by UV exposure and annealing as shown in Table 1. Previously reported hydrophilic/hydrophobic patterns are invisible so the result of surface treatment cannot be verified by a microscope [10], on the other hand, wettable/repellent pattern of PISC can be visually confirmed as shown in Fig. 3b.

![Fig. 3. (a) Water and tetradecane contact angle on PISC-X200 film as a function of UV dose. (b) Microscopic image of tetradecane droplets behavior on repellent area and 50-μm width of wettable area.](image)

**Fig. 3. (a) Water and tetradecane contact angle on PISC-X200 film as a function of UV dose. (b) Microscopic image of tetradecane droplets behavior on repellent area and 50-μm width of wettable area.**

![Fig. 4. Microscopic image of 10-μm width patterning of NPS-JL by inkjet with 1-pL nozzle on 10-μm width of PISC wettable patterns.](image)

**Fig. 4. Microscopic image of 10-μm width patterning of NPS-JL by inkjet with 1-pL nozzle on 10-μm width of PISC wettable patterns.**

### 3.2. Patterning of AgNP inks

High resolution metal line formation by two type Ag nanoparticle inks, NPS-JL (hydrophobic solvent dispersion) and Ag-JB1020B (aqueous dispersion) was achieved on wettable/repellent patterns by inkjet printing. We used 1pL of inkjet nozzle with NPS-JL, and the droplet diameter is ca. 15 μm. Considering ink spreading after impacting on substrates, the resulting metal line width will be estimated over 20-30 μm. However, owing to 10-μm width of wettable guide patterns of PISC-X200, 10 μm width silver lines formation was achieved by inkjet (Fig. 4).

An aqueous Ag nanoparticle ink Ag-JB1020B was also patterned by 1pL nozzle of inkjet with 20 μm of drop spaces. 10-μm width of fine silver line was obtained along PISC wettable line patterns shown in Fig. 5a and the thickness of resulting silver line was ca. 0.8 μm (Fig. 5b).

### 3.3. Source-drain electrodes patterning for OTFT

A top-gate, bottom-contact TFT device was manufactured using wettable/repellent control technique of PISC-X200 [11]. A channel length below 10 μm for TFT devices are generally required.
to achieve high-frequency performance of TFT arrays for displays and RFID tag devices [12-14]. However, it is difficult for printing process with metal inks to form this short channel width due to the printed ink spread. Schematic illustration of OTFT structure is shown in Fig. 6a. Source-drain electrodes were fabricated by inkjet coating of NPS-JL on patterned PISC-X200 as the target electrodes shape and 10μm of line width and channel length were achieved. Figure 6b shows uniformity difference of line width and channel length between on PISC pattern and on parylene layer without patterning. Inkjet coating of NPS-JL on parylene layer gave 221-233-μm range of line width and the average was 227 μm, a standard deviation was 2.4. On the other hand, significantly improved results, 8-12-μm range of line width, average 10 μm, standard deviation 1.0 were obtained on PISC pattern. Channel length uniformity was also greatly improved on PISC pattern. The fabricated OTFT device using this S/D electrode shows excellent transistor characteristics [11].

3.4. Formation of repellent template patterns

An alkali-soluble type PISC2 can be patterned by alkali-developer after UV exposure and baking in the same manner as positive tone photoresists [15-17]. Figure 7 shows SEM images of patterns of PISC-X007 with various film thicknesses,
resolutions and shapes. The resulting PISC patterns showed high repellency like PISC-X200 and the contact angle of water was 109°, while 20.3° on developed bare glass substrate surface. This high contrast of contact angle between repellent patterns and substrate makes it possible to self-patterning of functional inks same as undeveloped PISC1.

3.5. High aspect patterning by PISC template method

Here we show a novel high aspect patterning method using PISC repellent templates. Self-patterning of UV curable inks on the templates, followed by UV exposure for whole substrate and annealing make UV inks curing and PISC templates alkali-soluble. After alkali development, the templates were removed and cured UV ink was remained as a same shape of template holes (Fig. 8).

Figure 9 shows template patterning results of a conventional black pigment-dispersed UV ink (UV-IJ Black). UV-IJ Black was coated on 4, 8, and 10-μm width of wettable hole lines with 10-μm thickness by microcapillary, the ink was self-patterned in hole lines among lyophilic patterns. After UV curing and annealing, followed by template removing by alkali development, high resolution and aspect line patterns faithful with template size and shape could be formed.

High concentration titanium dioxide (TiO₂)-dispersed UV ink could be also patterned by PISC template method in the same manner (Fig. 10). The resulting pattern had 4-μm width, 5-μm height and the content of TiO₂ in film was over 80%. Formation of these black pigment or TiO₂-dispersed patterns with high resolution and aspect by photolithography technique is difficult because of light absorbance by carbon or light diffusion by TiO₂. Thus, PISC template process can provide a manufacturing method for forming structures difficult to be formed by a conventional technology.

3.6. Lens formation by PISC template method

Figure 11a shows a novel microlens formation scheme by PISC template method. Microlenses are utilized as a light focusing layer for optical devices like image sensors. In general, they are formed by photolithography patterning and following thermal Fig. 8. Schematic illustration of PISC template method.

Fig. 9. SEM image of black pigment-dispersed UV ink pattern by PISC template method.

Fig. 10. SEM image of TiO₂-dispersed UV ink pattern by PISC template method.

Fig. 11. (a) Schematic illustration of novel microlens formation method and (b) SEM image of resulting microlenses of 50-μm Φ and 100-μm Φ.
flow technique [18-20]. However, this method cannot be used for high film thickness lenses due to the limitation of applicable film thickness for photolithography. High thickness microlenses formation was successfully achieved by PISC template method. UV curable ink dropped by microcapillary on 0.5-μm thickness of round shape lyophilic templates gave hemispherical lens shape patterns and the UV ink can keep the lens shape by the repellent effect of template. After UV curing and annealing, followed by template removing, big size lenses with hemispherical shape could be formed (Fig. 11b).

4. Conclusion

In this study, we demonstrated an Ag line formation using PISC1 and the application to fabrication of source - drain electrodes for OTFT devices. Wettable/repellent pattern improved inkjet patterning resolution of AgNP inks and 10μm Ag lines were obtained with good uniformity and reproducibility. Furthermore, we showed a novel patterning method for high resolution, contrast patterns and microlenses. High resolution and aspect patterns of black pigment or TiO₂-dispersed inks and hemispherical high thickness microlenses of UV curable ink were formed by PISC template method. Those patterns and microlenses are difficult to be formed by conventional photolithography technique. We believe that these methods should be quite useful for manufacturing of advanced electronics devices hard to be fabricated using conventional methods.

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References

1. R. Sugano, Y. Takeda, Y. Kobayashi, K. Fukuda, D. Kumaki, and S. Tokito, Jpn. J. Appl. Phys., 52 (2013) 05DB05.
2. T. Arai, N. Sato, K. Yamaguchi, M. Kawasahi, M. Fujimori, R. Shiwaku, Y. Takeda, H. Hamaguchi, D. Kumaki, and S. Tokito, Bull. Chem. Soc. Jpn., 89 (2016) 424.
3. T. Igari and K. Yamaguchi, Chem. Lett., 46 (2017) 1220.
4. H. Matsui, Y. Noda, and T. Hasegawa, Langmuir, 28 (2012) 15450.
5. Y. Noda, H. Matsui, H. Minemawari, T. Yamada, and T. Hasegawa, J. Appl. Phys., 114 (2013) 044905.
6. M. Mori, Y. Mizutani, K. Yamamoto, S. Izumida, and H. Hitomi, IDW’12, 1489.
7. S. Yoshida, Y. Matsuura, N. Shiwaku, Y. Takeda, T. Sekine, H. Hamaguchi, D. Kumaki, and S. Tokito, J. Imag. Soc. Jpn., 59 (2020) 111.
8. E. Cantatore, T. C. T. Geuns, G. H. Gelinck, E. van Veenendaal, A. F. A. Grujthuijsen, L. Schrijnemakers, S. Drews, and D. M. de Leeuw, IEEE J. Solid-St. Circ., 42 (2007) 84.
9. J. A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crane, V. R. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing, and P. Drzaic, Proc. Natl. Acad. Sci. U.S.A., 98 (2001) 4835.
10. M. Mizukami, N. Hirohata, T. Iseki, K. Ohtawara, T. Sada, T. Yagyu, T. Abe, T. Suzuki, Y. Fujisaki, Y. Inoue, S. Tokito, and T. Kurita, IEEE Electron Device Lett., 27 (2006), 249.
11. M. Hasegawa, Y. Tanaka, K. Koseki, and A. Tominaga, J. Photopolym. Sci. Technol., 19 (2006) 285.
12. M. Yu, H. Xu, V. Kosma, J. Odent, K. Kasahara, E. Giannelis, and C. Ober, J. Photopolym. Sci. Technol., 29 (2016) 509.
13. J. Yu, N. Xu, Z. Liu, and L. Wang, ACS Appl. Mater. Interfaces, 4 (2012) 2591.