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Inkjet-Printed Lines with Well-Defined Morphologies and Low Electrical Resistance on Repellent Pore-Structured Polyimide Films

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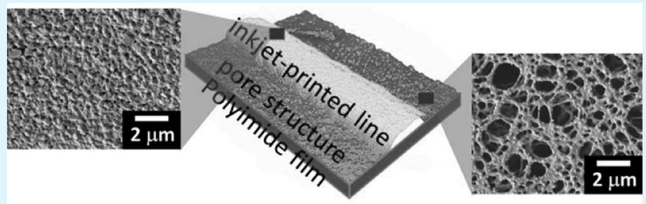
ABSTRACT: Polyimide films are the most promising substrates for use in printed electronics because of their high thermal stability. However, the high wettability of polyimide films by conductive inks often produces thin inkjet-printed lines with splashed and wavy boundaries, resulting in high electrical resistance of the lines. To overcome these disadvantages, we fabricated repellent pore structures composed of polyamideimide with high thermal stability on a polyimide film. Using this film, the inkjet-printed line thickness was increased without penetration of silver nanoparticles into the pore structures, thus resulting in very sharp edges without any splashing. This was because the repellent treatment restricted the spreading of the silver nanoparticles into the pore structures and the pore structures prevented ink splashing upon impact on the film. As a result, the electrical resistance of these lines decreased to one-fifth that of the lines on the pristine polyimide film. The inkjet printing of conductive inks onto repellent pore structures would contribute to the future of printed electronics because this technique enables printing closely packed line patterns while maintaining high conductivity within a limited space.



KEYWORDS: *inkjet printing, silver nanoparticle ink, silver conductive line, pore structure, fluorine treatment*

INTRODUCTION

Printed electronics is a promising technology that has received much interest for mass-produced, low-cost electronic devices because it increases manufacturing flexibility and decreases manufacturing costs. Among the numerous printing technologies such as offset printing, gravure printing, screen printing, inkjet printing is particularly advantageous as a noncontact, maskless, drop-on-demand process with scale-up feasibility. Therefore, inkjet printing is currently used to fully or partially fabricate advanced electronic devices such as organic light-emitting diodes,[1−3] organic solar cells,[4,5] organic thin-film transistors,[6−11] flat panel displays,[12] and radio frequency identification[13] devices. One of the key factors in improving device performance is the ability to print highly conductive line patterns with fine intervals on flexible plastics by using an inkjet printer.

Silver has a resistivity of 1.59 $\mu\Omega$ cm and is one of the materials with the lowest electrical resistance. Thus, silver nanoparticle-based conductive inks have been developed, and they can create high conductive patterns approximating bulk silver.[14−16] In most of these inks, the silver nanoparticles are capped by dispersants to improve their storage life. To remove these nonconductive dispersants, the printed line patterns are heated to extremely high temperatures greater than 200 °C.[17] As a consequence, thermally sensitive plastic films such as polyethylene terephthalate, polypropylene, and polycarbonate could not be used as substrates for printed electronic devices. On the other hand, polyimide films are the most suitable candidate substrates because of their high thermal stability.

When silver nanoparticle ink is inkjet-printed onto polyimide films, the characteristics of the substrates or inks often hinder obtaining highly conductive line patterns with fine intervals. The low viscosity of silver nanoparticle ink results in its inhomogeneous evaporation, thus inducing the "coffee-ring effect" within the printed lines. Consequently, the inhomogeneous distribution of silver nanoparticles increases the resistance of the lines.[18,19] The low concentration of silver nanoparticles in the ink decreases the printed line thickness after drying.[20] The high wettability of polyimide films also decreases the printed line thickness because silver nanoparticle ink droplets spread laterally on polyimide films.[21−23] Such thin lines induce high resistance because of their small cross-sections, even if printed lines with low resistivity are fabricated. Therefore, inkjet printing technologies using silver nanoparticle ink on polyimide films must print thick lines with low electrical resistance.

In this study, we aim to inkjet print well-defined, low electrical resistance lines with silver nanoparticle ink on polyimide films. To maintain the high thermal stability of the polyimide films, we fabricated fine pore structures on their surface using polyamideimide. Decreasing the pore diameters prevented the lateral spreading of the silver nanoparticle ink on the substrate surface. Moreover, fluorine treatment of the pore structures increased the thickness of the printed lines. Using the

Received: January 28, 2012
Accepted: March 27, 2012
Published: March 27, 2012

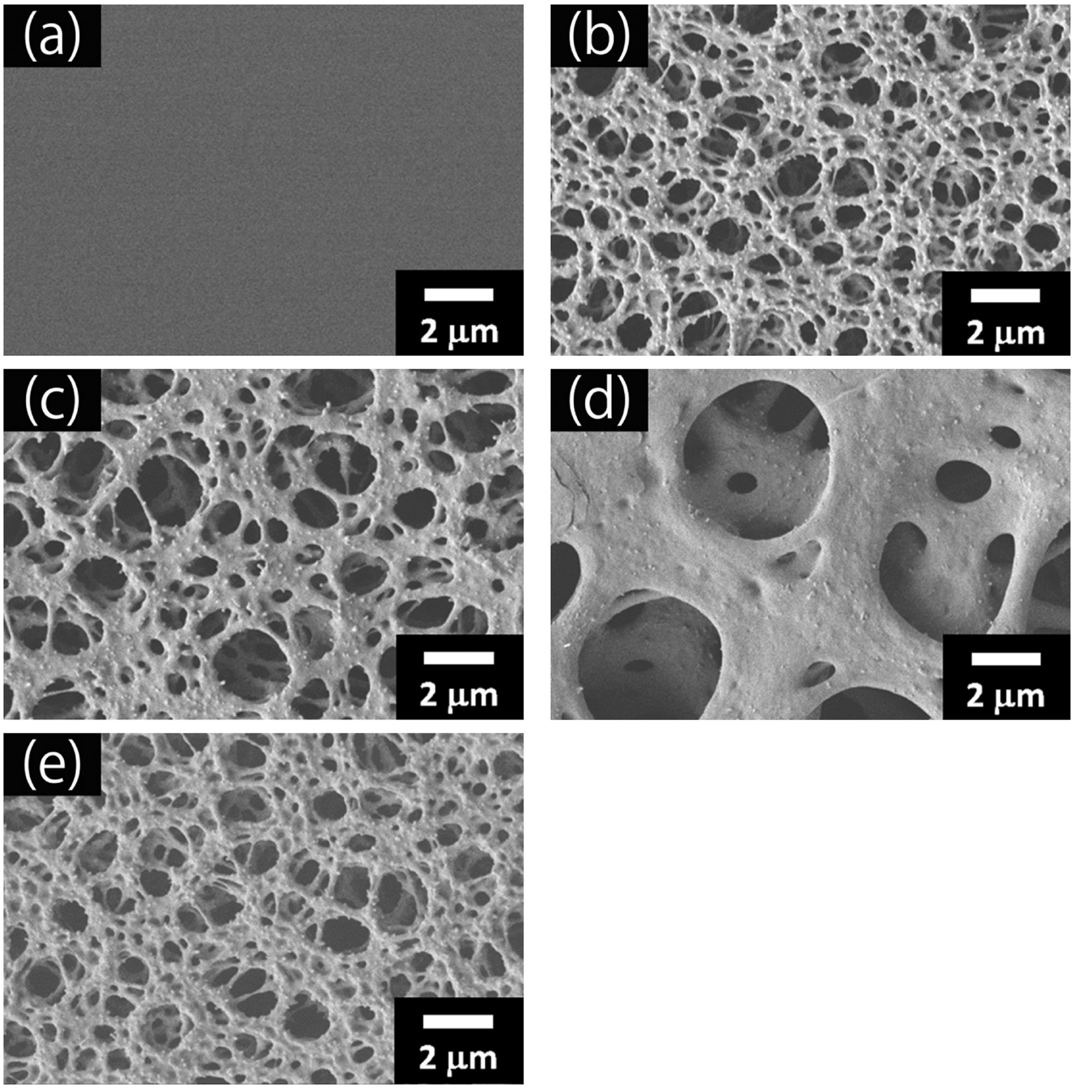


Figure 1. FE-SEM images of surface morphology on different substrates: (a) pristine polyimide film, polyamidimide pore-structured film with (b) 0.5 μm, (c) 3 μm, (d) 5 μm pores, and (e) fluorine-treated, polyamidimide pore-structured film with 0.5 μm pores.

repellent pore-structured polyimide films decreased the electrical resistance to one-fifth that of the lines on the pristine polyimide film, although the same silver nanoparticle ink, heating conditions, and dimensions (line width and length) were used.

■ EXPERIMENTAL SECTION

Silver Nanoparticle Ink and Polyimide Base Substrates. The silver ink used in this work was a commercially available silver nanoparticles ink in tetradecane (NPS-J type HP, Harima Chemicals, Inc., Japan). The ink contained 62−67 wt % silver nanoparticles with an average diameter of 12 nm. A polyimide film substrate (Figure 1a; Kapton 200H, DU PONT-TORAY CO., LTD, Japan) with 50 μm thickness and three surface-modified polyimide films were used as the printed substrates. The surface-modified films were polyamidimide pore structured (Figures 1b−d), fluorine-treated polyamidimide pore structured (Figure 1e), and fluorine treated without pores. The thickness of the pore structures was 25 μm and the pore sizes were 0.5, 3, and 5 μm.

Inkjet Printing. Inkjet printing was performed with a piezoelectric system (Dimatix DMP 2831, Dimatix-Fujifilm Inc., USA) equipped with a 10-pL cartridge (DMC-11610). The silver nanoparticle ink was printed at a voltage of 22 V and a frequency of 5 kHz using a customized waveform. An array of droplets (2000 × 1) was deposited with a dot-to-dot spacing of 20 μm and resulted in printed lines of length 40 mm.

Ink droplets were overprinted thrice onto the previously formed dots. The substrate was kept at room temperature during printing; the distance between the substrate and nozzle was set to 1 mm. After printing, the printed lines were heated at 220 °C for 60 min in air.

Characterizations. The contact angle formed by the sessile ink droplet after 3 s of impact on the different substrates was measured using a contact angle analyzer (Drop Master 300, Kyowa Interface Science Co. Ltd., Japan) along with a Teflon-coated needle (No. 511) and a glass syringe (No. 586). Using 4-μL ink droplets, seven sets of measurements were performed at different locations on the fabricated substrates and then averaged. The printed lines were examined by field emission scanning electron microscopy (FE-SEM; JSM-6700F, JEOL Ltd., Japan) at an accelerating voltage of 5.0 kV and a working distance of 7−8 mm, or with a 3D microscope (VK-9500, KEYENCE, Japan). The electrical resistance of the printed lines was measured by the four-point probe method (34410A, Agilent, USA). Four probe pads (1 × 1 mm^2) were fabricated on the printed lines at 5-mm intervals by gold sputter deposition (Mild Sputter E-1045, Hitachi High-Technologies Corp., Japan).

■ RESULTS AND DISCUSSION

Polyimide films have been widely used as substrates in printed electronics because of their high dimensional stability against high sintering temperatures over 200 °C. However, when conductive inks are inkjet-printed on these films, their high surface energy of 40 mN/m often results in wide-spreading thin lines.[21] In this study, silver nanoparticle ink with a tetradecane solvent was used. At impact, the 4-μL droplets of the silver nanoparticle ink spread laterally on the polyimide film. Their contact angles were only 11° (Figure 2a). Thus, inkjet printing on the polyimide film yielded splashed lines with wavy boundaries (Figure 2b). The lateral spreading of the ink droplets decreased their thickness to less than 0.3 μm and resulted in lines with various widths 70−140 μm and length 40 mm (Figure 2c). Because of the high thermal stability of polyimide films, the printed lines were subjected to heat sintering conditions at 220 °C for 60 min. Consequently, the inkjet-printed lines exhibited a low electrical resistance of 5 Ω. This was 2.6 times the resistance of bulk silver by considering the line volume and resistivity of silver (1.59 $\mu\Omega$ cm). Because these printed lines were subjected to sufficient sintering conditions, their resistance could not be decreased further even with prolonged heating or a higher temperature. However, increase in line thickness decreases their resistance using the same ink, line width, and sintering conditions. Increase in ink viscosity is effective for increasing line thickness; however, high viscosity ink is difficult to inject through an inkjet printer. Thus, surface modification of substrates is a practical way to increase line thickness.

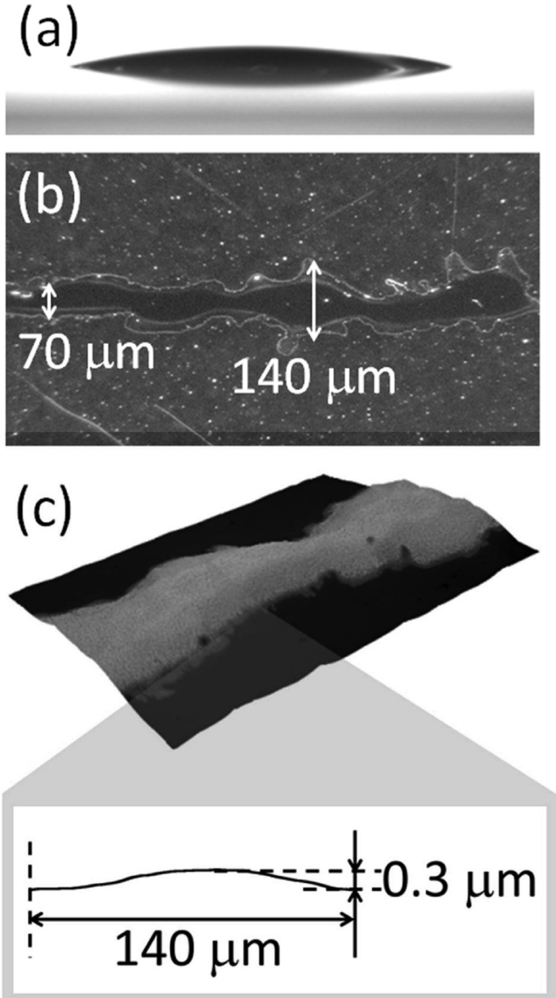


Figure 2. Pristine polyimide film: (a) Contact angle of the 4-μL silver nanoparticle ink droplets, inkjet-printed line morphology: (b) top view and (c) 3D view.

To increase line thickness, we fabricated pore structures on the polyimide film. Pore structures have been used in screen printing to obtain thicker lines with sharp edges.[24,25] In this study, the pore structures were composed of polyamidimide in order to maintain the high thermal durability of the printed substrates. Similar to polyimide, polyamidimide also has high thermal stability, and their glass transition points are around 300 °C. The contact angle of the silver nanoparticle ink droplets on polyamidimide was 9.5°. Thus, their wettability was similar to that on the polyimide films. According to Wenzel's equation, such a spreadable surface becomes more spreadable with pore structures.[26] When the 4 μL ink droplets were impacted on the pore-structured films with 0.5, 3, and 5 μm pore structures, the droplets were absorbed into the pore structures. Therefore, their contact angles could not be measured, as shown in Figure 3.

Figure 3. Contact angle of the 4 μL silver nanoparticle ink droplets on the polyamidimide pore-structured film.

As described above, the inkjet-printed lines with silver nanoparticle ink on the polyimide film resulted in splashed and wavy boundaries (Figure 2b, c). In contrast, when the silver nanoparticle ink droplets were inkjet printed on the polyamidimide pore-structured film, the ink wetted the surface and then was absorbed into the capillary network. As a result, the printed lines on the pore structures reduced the splashing and the edges became sharply defined (Figures 4a, 4b, 5a). However, on the film with large pore structures (5 μm), the printed lines spread laterally and their width of 300 μm was twice that on the pristine polyimide films (Figure 4a). Shrinking the pore size could reduce the spreading of the printed lines. Decreasing the pore size to 3 μm resulted in a narrower line width of 150 μm, which was equivalent to the width of the lines on the pristine polyimide films (Figure 4b). The smallest pore size of 0.5 μm produced a 50-μm-wide line because the silver nanoparticle ink droplets had difficulty spreading laterally into the fine pore structures across the large surface area (Figure 5a). Therefore, such fine pore structures prevented the splashing and spreading of the silver nanoparticle ink, resulting in narrow lines with sharp edges. However, the silver nanoparticle ink was completely absorbed into the substrates, resulting in a flat surface (Figure 5b). This result is similar to that of the contact angle measurements shown in Figure 3. FE-SEM examination of the printed lines revealed many cavities due to the ink penetration along the pore structures (Figure 5c). As a result, the electrical resistance of the lines was 25 Ω, even after sufficient sintering conditions of 220 °C for 60 min. This electrical resistance was five times larger than that of the lines on the pristine polyimide films.

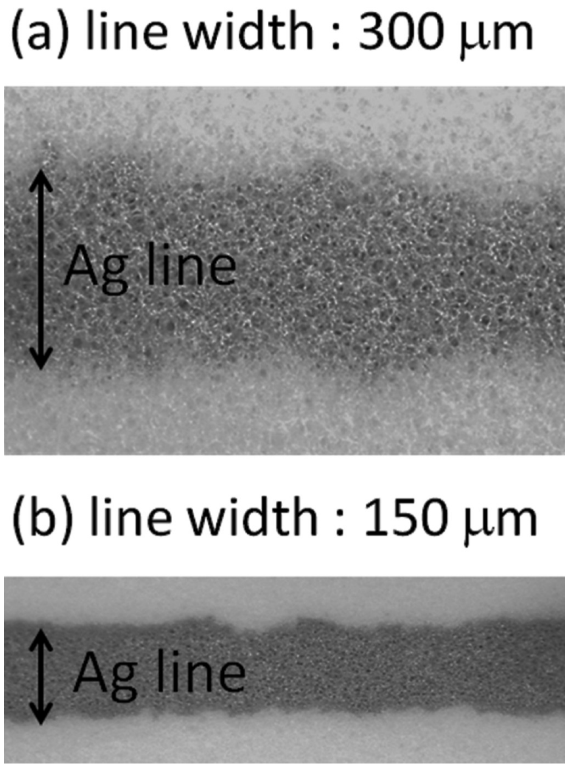


Figure 4. Laterally spreading inkjet-printed lines with silver nanoparticle ink on the polyamidimide pore-structured films with (a) 5 and (b) 3 μm pores.

The fine pore structures produced narrow lines with sharp edges, but they resulted in the drawback of low electrical conductivity due to the absorption of the silver nanoparticle ink droplets. Therefore, to avoid the penetration of the silver nanoparticle ink droplets into the pore structures, the polyimide films with 0.5-μm pore structures were chemically modified with fluorine treatment. Then, the 4-μL silver nanoparticle ink droplets were dropped on the fluorine-treated polyimide films with and without pore structures. The contact angles on the fluorine-treated polyimide film with and without pores were 95 and 98°, respectively (Figures 6a, 7a). Both fluorine-treated substrates exhibited almost the same degree of repulsion against the 4 μL ink droplets. Surprisingly, significantly different line patterns were obtained on these substrates through inkjet printing.

The silver nanoparticle ink droplets were inkjet printed on the fluorine-treated films with pore structures. As shown in Figure 1b, e, it is obvious that there was no difference between the surface morphologies with and without the fluorine treatment of the pore structures. The pore structures were not filled with fluorine treatment substances. The pore structures did not absorb the droplets and the silver nanoparticles remained on the surface of the fluorine-treated pore structures owing to their repellent property induced by the treatment. (Figure 6d). In this case, the printed line thickness increased to 1.0 μm (Figure 6c), resulting in a narrower width of 30 μm with sharp edges (Figure 6b). The fluorine-treated pore structures yielded well-defined lines that were more than three times thicker than those on the pristine polyimide films. Moreover, the printed lines on the fluorine-treated pore structure films exhibited a resistance of 8 Ω because the silver nanoparticles remained on the pore structures. This resistance

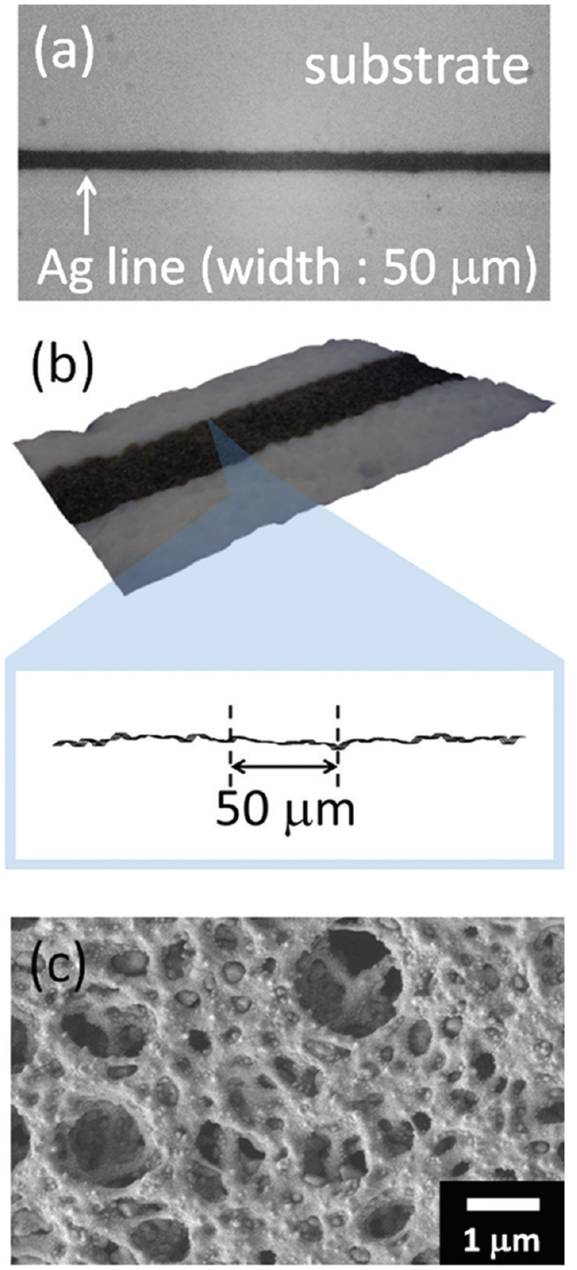


Figure 5. Inkjet-printed lines on the polyamidimide pore-structured film with 0.5 μm pores: (a) top view, (b) 3D view, and (c) FE-SEM images of silver nanoparticles after sintering.

is almost equal to that on the pristine polyimide films. In contrast, when the silver nanoparticle ink droplets were printed on the fluorine-treated polyimide films without pores, the droplets were effectively repelled and remained on their surface and became dotted lines with 40 μm diameter and 1.6 μm thickness (Figure 7b, c). This resulted in no conductivity.

At the same line width and length, increasing the line thickness decreases the electrical resistance of the printed lines. Therefore, the silver nanoparticle ink droplets were inkjet printed on the repellent pore-structured polyimide films in order to obtain lines with the same dimensions as those on the pristine polyimide films, i.e., 140 μm width and 40 mm length. As shown in Figure 8, we succeeded in printing rectangular lines with a large thickness of 1.0 μm because of the repellent pore structures. This thickness was three times that of the 0.3

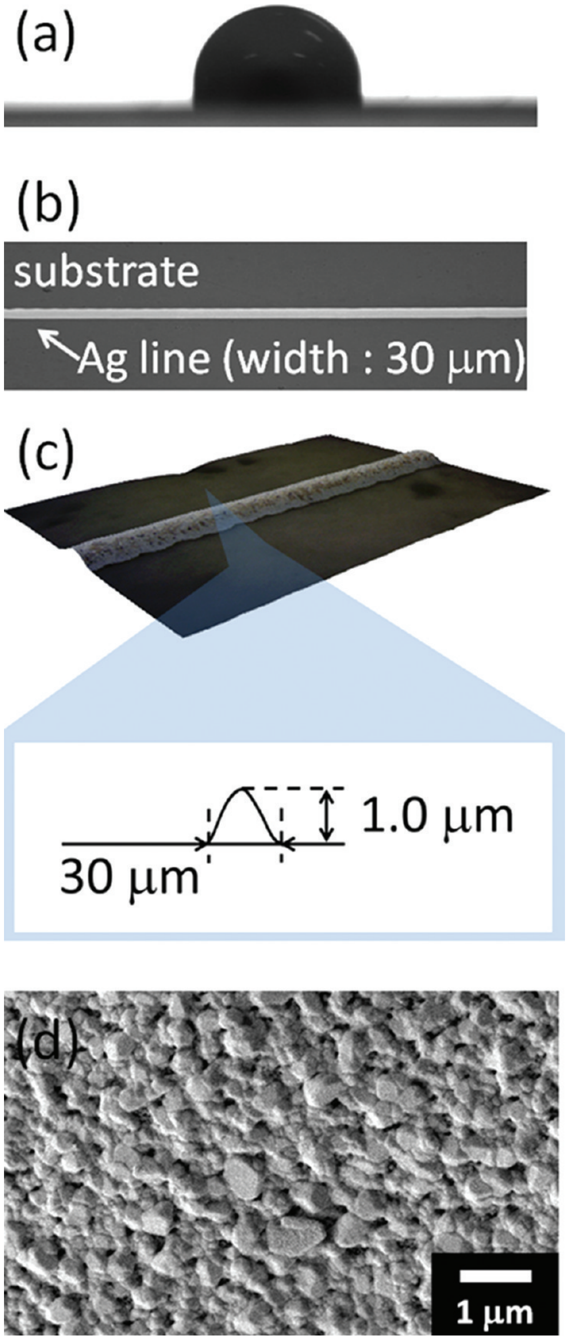


Figure 6. Fluorine-treated polyamidimide pore-structured film with 0.5 μm pores. (a) Contact angle of the 4 μL silver nanoparticles ink droplets. Inkjet-printed line morphology: (b) top view, (c) 3D view, and (d) FE-SEM images of silver nanoparticles after sintering.

μm line thickness on the pristine polyimide films. As a result, the electrical resistance of the thicker lines was decreased to only 1 Ω, although that of the thinner lines on the pristine polyimide film was 5 Ω. Moreover, the lines showed sharp edges without any splashing, indicating that fine interval lines with close gaps could be printed on the repellent pore-structured polyimide films. Therefore, inkjet printing on the repellent pore-structured film could produce closely packed line patterns with high conductivity within a limited space. In the future, printed electronics such as tiny sensor tags, high-power conversion solar cells, high-speed computers, and flexible displays will be possible with the technique.

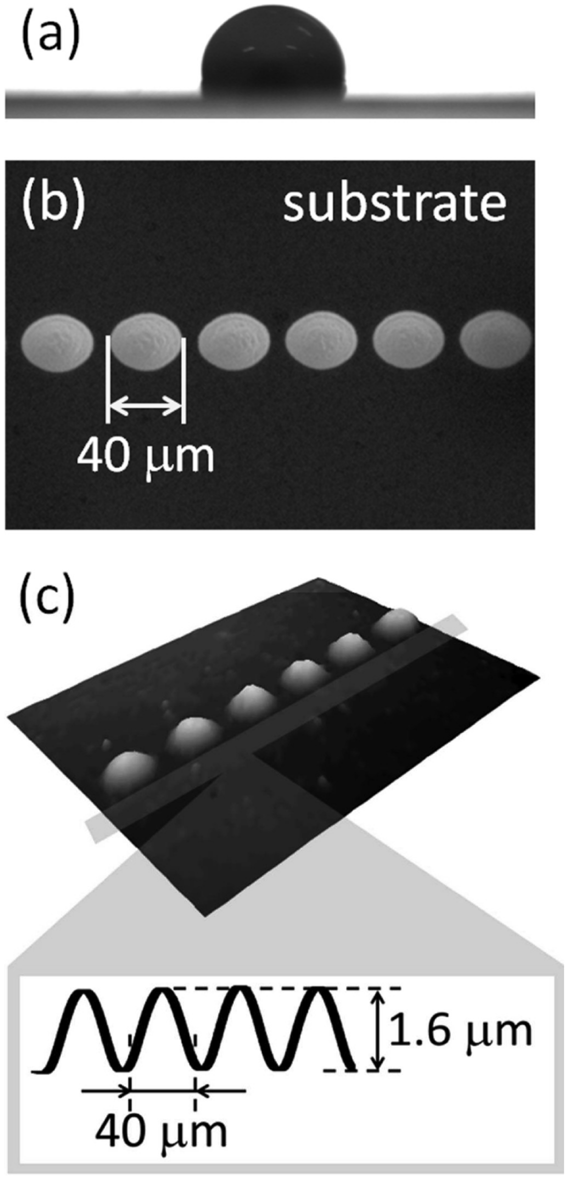


Figure 7. Fluorine-treated polyimide film. (a) Contact angle of the 4 μL silver nanoparticle ink droplets. Inkjet-printed line morphology: (b) top view, and (c) 3D view.

■ CONCLUSION

Silver nanoparticle ink droplets with a tetradecane-based solvent were inkjet printed onto polyimide films. Because of the high wettability of polyimide films, the inkjet-printed lines had a rough shape with laterally spreading, splashing, wavy boundaries and low thickness. Pore structures were fabricated using polyamideimide on the polyimide films. When the silver nanoparticle ink droplets were inkjet printed onto the pore-structured polyimide films, the pore structures prevented the splashing of the silver nanoparticle ink droplets at impact. Using fine pore structures of 0.5 μm yielded narrow lines with sharp edges. However, their electrical resistance was five times that of same length lines on pristine polyimide films because the silver nanoparticles were absorbed into the fine pore structures. Then, the pore structures on the polyimide films were chemically modified with fluorine treatment. The obtained repellent pore structures restricted the spreading of the silver nanoparticles into the pore structures and resulted in thicker

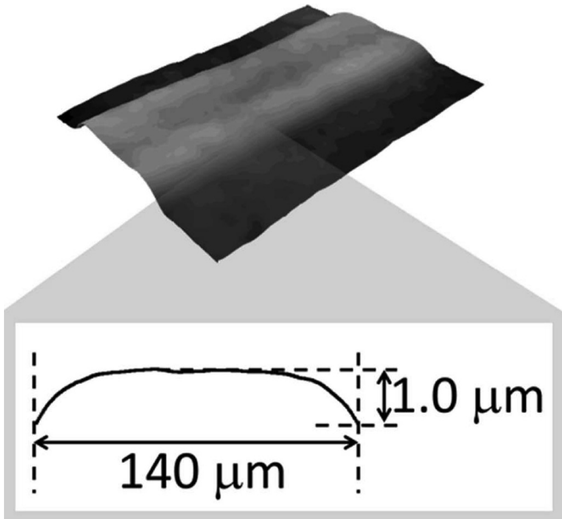


Figure 8. Highly electric conductive inkjet-printed line on fluorine-treated polyamidimide pore-structured film.

lines while maintaining their sharpness and decreasing their width. When the silver nanoparticle ink droplets were inkjet printed onto the pristine polyimide films, the printed line width was about 140 μm. Next, lines of this width were inkjet printed onto the repellent pore-structured polyimide film. In this case, the electrical resistance of the 140 μm wide printed lines was decreased to one-fifth that of those on the pristine polyimide films. This was because their thickness increased from 0.3 to 1.0 μm.

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Notes

The authors declare no competing financial interest.

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