Inkjet Patterning of UV Curable Etching Resist for Flexible Conductive Circuit Electrodes

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Abstract

This paper discloses the recent evolution of flexible substrates with conductive film patterns by use of inkjet patterning of UV curable resist, etching process, and then striping the resist film in sequence. The UV curable ink has a viscosity of about 8~20cps and surface tension of 30~40 dyne/cm at operation temperature, which is appropriate for the inkjet printing process conducted on the ink at an elevated temperature. Experimental results indicated that the single drop size on the conductive film is about 75~80µm. For the continuous line pattern, the minimum line width and line spacing of the printed resist can reach from 80 µm /60 µm to 80 µm/ 20 µm, and the resist thin film thickness is 5µm. After the etching and striping process, the conductive line width and line spacing can be 80 µm/ 20 µm. This low-cost and easy process is potentially promising to flexible electronics in the future.

Introduction

There are many traditional methods for patterning conductive circuit and electrodes in industry, such as photolithography, screen-printing, spin-coating, laser direct imaging (LDI), etc. Screen-printing and photolithography are the dominant manufacturing methods for imaging conductive features. These processes can use liquid or dry type photoresist as the masking layer. These techniques have served the industry well because they provide acceptable image resolution at a reasonable material cost. However, they still suffer the drawback of being analogue processes and they require expensive equipment with high precision, photo masks, and complicated multi-step procedures. These prolong the delivery time of samples and prototypes to customers.

In the LDI process, an expensive, special, dry film is always necessary for use as the etching resist material. In addition, a complicated laser system is used as the exposing light source and for writing the circuit pattern directly onto the etching resist. Although it does not need a mask and can provide high resolution pattern, the writing speed is extremely slow, and the cost per panel is very high with this technology. \(^1\)

In recent years, printed organic electronics have been developing intensively because of the many advantages for a variety of low cost and large-area electronic applications, such as polymer light-emitting diodes (PLED), organic thin-film transistors (OTFT), liquid crystal displays (LCD), bio-sensors, organic bi-stable memory (OBD), as well as metal circuits (printed circuit board (PCB) and radio frequency identification (RFID)). According to the forecast data from marketing research institutes, printed logic integrated circuits are gradually attracting a great deal of attention and will dominate in the future. 2.3

The physical properties of UV-cure materials are substantially affected by the UV curing system. There are four major factors to consider to gain the optimal curing material properties - UV transmittance of the material, spectral distribution (max. wavelength and wavelength distribution) of the UV source, UV light energy, and infra-red radiation. The influence will be reflected on adhesion, solvent resistance, etching resistance, striping ability, and scratch resistance. Suitable UV-system and process flow for a UV curable material yields more efficient and stable curing results in ink-jet printing.^{4,5}

The basic components of UV-cure ink are monomers, oligomers, photo-initiators, colorants (dye or pigment), and some additives (surfactant). The monomers are small organic molecules which will dominate the viscosity, rheology, surface tension, and curing speed of the UV ink. In addition, it will also influence the resulting polymer structure, and therefore the chemical resistance. Oligomers are larger molecules, essentially high molecule weight acrylic resins, which act as binders and will determine the basic properties of the UV cured layer (flexibility, adhesion, hardness, and resistance). The photo-initiators absorb UV energy to start a radical polymerization to afford fully cured film. The concentration and the initiated wavelength of a photo-initiator, therefore, are important in determining the curing speed and level of curing. The additives in inkjet printing ink were to control ink viscosity and surface tension, and to enhance additional printing stability6

In this paper, we report on a process of fabricating flexible conductive circuit electrodes by inkjet printing. The effect of the image trimming method and substrate surface cleanness is described in detail.

Experimental Section

Substrate Cleaning

The cleanness of substrates is very important to ink-jet print patterning. Some particles and greasy dirt on the substrate surface would change the surface free energy, contact angle, and surface flatness. Before printing etching resist, substrates were cleaned by two different methods as shown in Table 1.

Table 1: Substrate cleaning parameters

Manual cleaner	Semi-automatic cleaner
IPA for 10min	Only detergent and DI
DI Water for 10min	water with sonication in
Ethanol for 10min	sequence
DI Water for 10min	

Image Trimming

The wetness of ink on the landing substrate is crucial to the size of pattern. Based on the landing behavior, we use the image modification module with the landing resulting parameters to trim the printed pattern to reach high quality patterns. The line width and spacing can be well controlled.

Ink Properties

In Table 2, the physical properties of a solvent free UV curable etching resist are described. The specification fits most commercial piezoelectric (PZT) print heads.

Table 2: Properties of the solvent free UV cure etching resist ink

Viscosity	12cps@45°C
Surface	25-28 dyne/cm
Tension	@25°C
Color	Black
Film	5-40 um
Thickness	

Ink-Jet Printing System

The self-integrated ink-jet printing system, equipped with commercial PZT heads, was used for ink patterning. This head has 128 nozzles, with a physical resolution of 50 dpi. The volume of a discharging droplet can be tuned from 15 to 35 pico-liters (pL) by changing the driving voltage and modulated waveform.

UV Curing Condition

The UV curing rate depends on the thickness of the printed etching resist. In this study, the thickness of the patterned resist was 5 um. It was then illuminated 3~5 sec with a 120 W UV lamp.

Etching and Stripping

In different etching liquids, the etching resist has an excellent endurance for several important conductive layers, including indium zinc oxide (IZO), copper, aluminum, etc.

The IZO/PC film, with resist pattern, was immersed into an oxalic acid aqueous solution of 2 % at room temperature, to remove the IZO layer that no resist covered. The etching rate was about 4.8A/sec. After the etching process, the substrate was dipped into DI water to remove the residual oxalic solution. Finally, the mask resist was stripped by immersion into a solution of 3% sodium hydroxide solution for 300 sec.

Result and Discussion

Substrate Cleaning

Although the normal cleaning method could clean the surface, this method could not obtain a uniform ITO surface. The optical microscopy photographs of printing pattern are shown in Fig 1. Fig. 1(a) and Fig. 1(c) and show manual operation. The line width varied from 80um to 150um as indicated by the red mark.

Besides, deckle, discontinuous line, zigzag, and tadpole shaped features were all observed. These defects were attributed to a non-uniform surface property caused by a few micro particles and greasy dirt. They would have changed the ink contact angle on parts of the IZO substrate surface tension, and therefore influenced the settled position of printed ink. In the case of the semi-automated cleaner, the printing results are shown in Fig. 1(b) and Fig. 1(d). The line width variation was below 5%. In this case, the ink aggregation problem had been mitigated, and the line edge was smooth, too.

As shown in Fig. 1(c), (d), (e), and (f), there were discontinuous and necklace-like defects in the diagonal line and vertical line. The cause of these problems needs to be identified further in the future. It is believed that interaction of the etching resist ink and the IZO substrate surface will prove to be an important factor of this phenomenon. The duration of the successive landing drops on the vertical and diagonal line was larger than that of the printed line parallel to the printing direction. The ink and ink attraction was larger than that of the ink and substrate surface. Part of the ink aggregated and became tadpole-like shapes (Fig. 1 (e) and (f)), and the etching resist ink also shrunk to form gaps (Fig. 1 (d)).

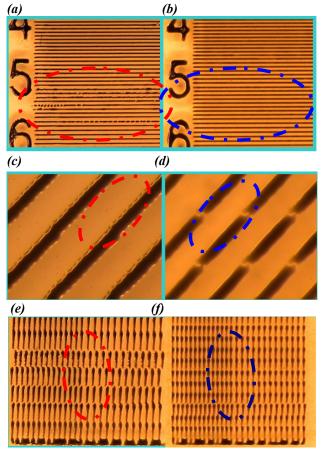


Fig.1 (a), (c), and (e) show the use of the Manual cleaner substrate cleaning process. In this process, the quality of the lines was not uniform. Fig.1 (b), (d), and (f) show the use of the Semi-automatic cleaner cleaning process. Here the quality of lines was uniform.

Image Trimming

The input original and trimming images are shown in Fig.2 (a) and (b), respectively. The line width and spacing was 80/20, 80/40, and 80/60 (um/um). For the original high resolution image, high dot density was used. The corresponding printed results are shown in Fig. 3 (a), (c), and (e). The printed patterns smeared and became a continuous area in the 80 um/ 20um case. Some linking defects by the line width and the line space were also observed for 80 um/ 40 um and 80 um/60um cases. In addition, the printing result of line width was larger than the original design because of too many droplets on the substrate. For the trimming image, a lower dot density and high resolution were used. The results are shown in Fig. 3 (b), (d), and (f). The printed line width/space did not smear out and matched the trimming design for all three specifications.

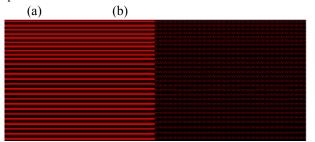


Fig. 2 (a) was an original image and (b) was a trimming image. The line width and line space were design 80/60, 80/60 um, and 80/20 um.

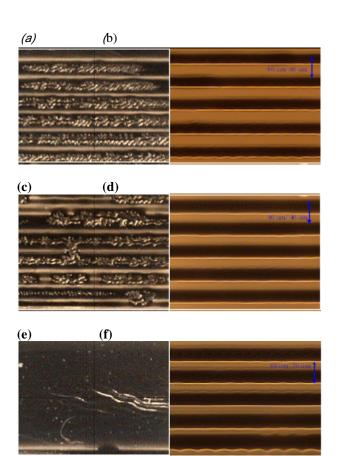


Fig. 3 (a), (c), and (e) were the resulting patterns of printing original image on flexible IZO substrate, and (b), (d), and (f) were the resulting patterns of printing image trimming on flexible IZO substrate.

Etching and Striping

Before etching, the etching resist thickness and profile were measured by α -Step, as shown in Fig. 4 (a) and (b). The etching resist thickness of each line was about 5 um, and line width was 80um on an IZO substrate. The profile was similar and uniform.

After striping, the IZO thickness and profile were also measured by $\alpha\text{-Step}$, as shown in Fig. 5 (a) and (b). No residual resist was observed on the IZO surface. The IZO surface was very uniform, indicating the etching liquid cannot permeate into the etching resist film. The IZO pattern was well defined with no undercut.

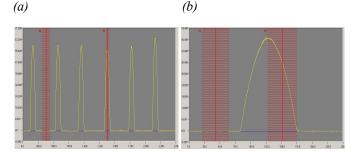


Fig. 4 Etching resist thin film thickness analysis by α -Step measurement was 5 um and the line profile was uniform by etching resist pattern.

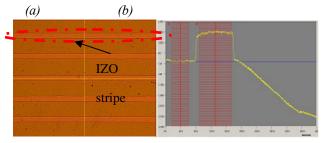


Fig. 5 IZO flexible conductive thin film thickness analysis by α -Step measurement was 170 nm. The entire line profile was uniform.

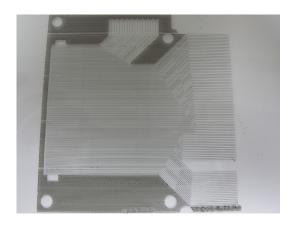


Fig. 5: An IZO flexible conductive circuit LCD electrode.

Conclusions

In this paper, we have successfully applied inkjet printing to fabricate a flexible IZO conductive circuit electrode (Fig. 5) by the use of UV curable etching resist ink. We demonstrated that printing quality, such as line width control, edge uniformity, and tadpole-like defect reduction, can be improved by use of different UV curing and image trimming methods. In order to further enhance the pattern quality, the real time UV curing process will be preferable in the future.

References

- Mark James, "Photochemical Machining by Ink Jet A Revolution in the Making. " IS□T's NIP20: International Conference on Digital Printing Technologies, PP. 279-283, 2004
- Kevin Cheng , Ming-Huan Yang, Wanda W. W. Chiu, Chieh-Yi Huang, Ja ne Chang , & Tai-Fa Yin, "Ink-jet printing, self-assembled polyelectrolytes, and electroless plating: Low cost fabrication of circuits on flexible substrates at room temperature." MRC Vol. 26, PP. 247-264, 2005
- 3. D. Redinger, R. Farshchi, and V. Subramanian, "Inkjetted Passive Components on Plastic Substrate for RFID", to be presented, IEEE Device Research Conference.,2003
- R. W. Stowe, R. W. "PRACTICAL Relationships Between UV Lamps and the UV Curing Process Window," Proceedings, RadTech North America; 1994
- R. W. Stowe, "Effect of UV Exposure Conditions on Speed, Depth Cure and Adhesion," Proceedings, RadTech North America; 2002
- 6. R. W. Stowe, "Key Factor of UV Curing of Ink Jet Printing" IS□T's NIP19: International Conference on Digital Printing Technologies, PP.186-189, 2003

Biography

Chung-Wei Wang received his Masters degree in the Institute of Organic and Polymeric Materials from National Taipei University of Technology in 2004. He is now a process engineer in the Printing Science Department, Panel Integration Division II, Display Technology Center of Industrial Technology Research Institute at Taiwan. His work has primarily focused on the industrial ink-jet printing processes development, especially in LCD, PCB, and new electronics application.