A Novel Primer Coating on Organic Substrate for Reliable Inkjet Printed Circuit

Minsu (Tim) Lee* Younghoon Kim and Youngwook Kim
R&D Center, Doosan Cooperation, Electro-Materials BG
Yongin, S. KOREA

Abstract

Even though ink jet printed circuit has many advantages over typical subtractive PWB technology such as fewer processes, less waste and labor, it has some problems. A major problem is weak adhesion between circuit and substrate. The other problem with ink jetting conductor is poor line and edge quality. One of the most widely adapted solutions is the substrate surface treatments. The various treatment methods have been used to increase the affinity between substrate and ink. However, the resulting circuit quality was still not good enough to be compatible with conventional circuit. Therefore, printed electronics industry is looking for new method.

To meet this demand, a novel primer coating technology is developed. An aromatic primer was spin coated and dried on either Fr-4 or PI substrate. The contact angle between nano silver ink and the coated surface has been increased more than three times to 50~70 degrees, resulting in quality ink jet printing. The line definition and edge quality of 100um/100um circuit after sintering was as good as those of conventional circuit. Fine pattern up to 25um/25um was possible using 10um nozzle. The adhesion by newly developed peel test method was 1~1.5 kgf/cm2, which is compatible with conventional PWB. The reliability of printed circuit was also good. The details of peel test method and reliability test results will be presented.

Introduction

Printed circuit board (PCB) fabrication utilizes photolithography, which includes various process steps such as applying photoresist, light exposure, developing, plating or etching and stripping. These complicated and time-consuming processes result in high manufacturing costs due to costly equipment and electronics materials. Recently, inkjet printing has been considered as a promising alternative to conventional PCB fabrication, for it can reduce the amount of material waste in production, decrease the number of process steps, and consume less energy. It will affect the value networks and supply chains.[1~4]

Even though inkjet printing method has many advantages, it is not well adapted for electronic packaging industry because of some problems. The major problems are weak adhesion between circuit and substrate, poor printing quality and low reliability. To solve these problems, much effort has been put to ink and inkjet printer with limited success. Recently, there have been few reports showing that substrate treatment makes big impact on adhesion and printing quality. Surface energy seems to be a driving force for pattern quality. Various treatments have been performed to decrease the surface tension of substrate, which makes fine pattern possible.[5~9]

Treatments can be divided into two groups, which are dry process and wet process. One of the most widely used dry processes is plasma treatment. Plasma treatment with hydrophobic gas enables high quality fine pattern printing.

However, adhesion is still not strong enough for PCB application. Wet process such as simple coating with hydrophobic compounds needs additional heating of substrate after the treatment to have a positive effect. Heating can induce clogging of the nozzles, which can cause open circuits or satellite drops. Therefore, new wet treatment is needed for inkjet printed circuit process. The goal of this study is to develop newly treated primer for inkjet printed circuit and to evaluate the capability of the inkjet printing technology for inkjet printed circuit.

Experimental Procedure

Surface Treatment

Substrates such as FR-4 need proper treatments for high quality inkjet printed circuit. FR-4 is 800um thick without copper. To prepare coating solution, resin system including epoxy resins, hardeners and additives were mixed. dissolved and adjusted to 40 wt % in methyl ethyl ketone. Fig.1 shows structures of modified epoxy resins used in experiments. R is fluorocarbon. Primers were either spin or bar coated on 10 cm X 10 cm substrates. Coated substrates were dried at 120℃ for certain time and cooled before testing.

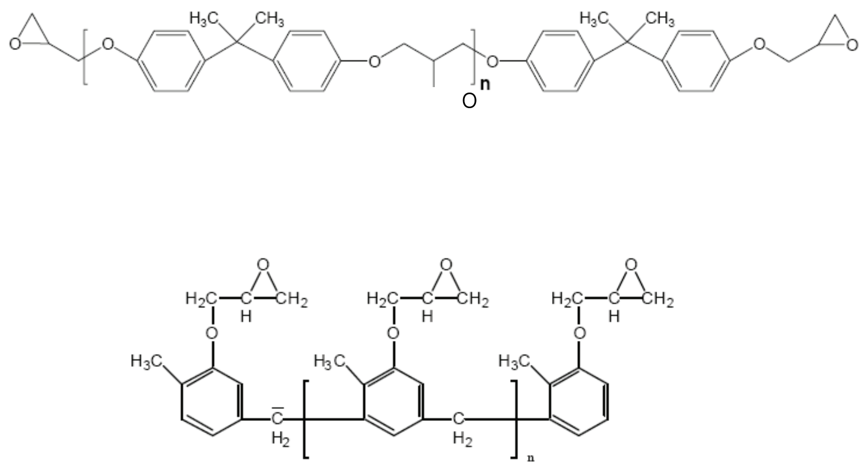


Fig 1. Structures of epoxy resins

Contact angle measurements

Contact angles of treated substrates were measured by DSA 100 (Kruss Hamburg, Germany) contact angle analyzer. Surface energy was calculated from contact angles of deionized water, formamide and diiodomethane.

The instrument consists of a microscope connected to a video camera. The sample is placed on a horizontal plate within a closed sample chamber, which can be moved in the x-y-z plane. The liquid droplet is placed on the sample with a gravimetrically calibrated micrometer syringe and the droplet contour is registered with the video camera. All contact angles were measured in air and the height and base of the droplet were registered. The contact angle was calculated from:

(1). $$\cos\theta = \frac{F}{L \cdot \sigma}$$

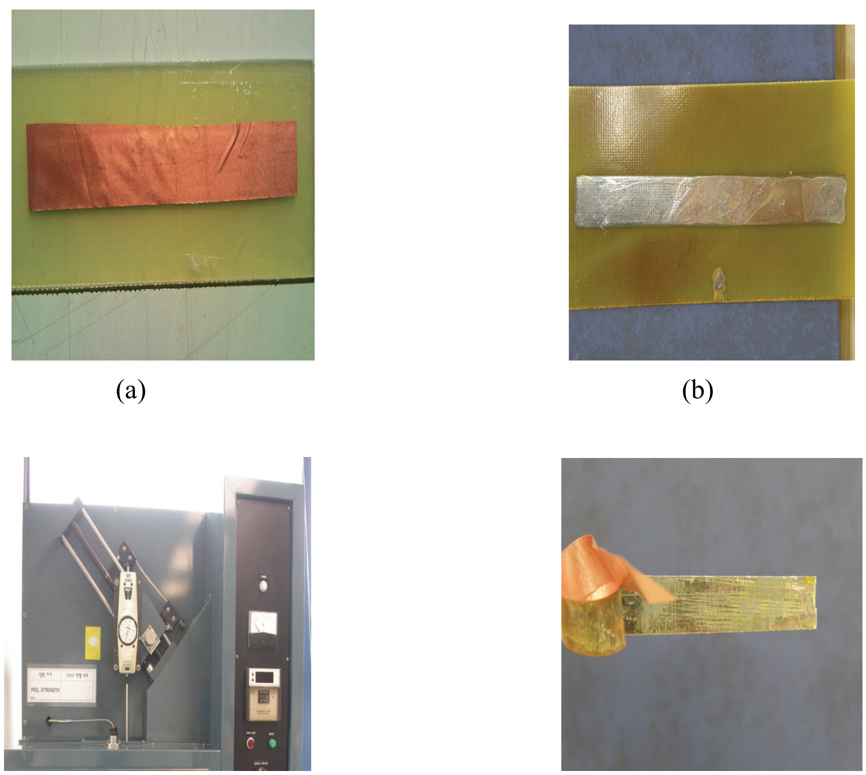
Where F is the wetting force, L is the witted length, σ is the surface tension, and θ is the contact angle. Contact angle was measured five times at different location on the surface by the sessile drop method. The average values were used for the analysis and calculation of surface energy from Wu's harmonic mean model [3]. Typically, measurements for same sample have a standard deviation of less than 2o.

Printing Process

The multi-nozzle system from Dimatix composed of piezo type cartridges with 10 picoliter 19㎛nozzle was used for ink jet printing. Nano Ag ink from ANP of S. Korea was inkjet printed on treated substrates at room-temperature. The ink has 35% of metal content in polar solvent and surface tension of 35dyn/cm2. The printed substrates were immediately loaded into a convection oven and were baked at 150℃ for 30min. The printed patterns in microscopic images were analyzed by Tomoro ScopeEye image analysis program V3.5 (Image Partnership Co., Ltd., Anyang, Korea).

Peel strength of inkjet printed circuit

Even though there is standard method for measuring peel strength of printed circuit, that method was not practical for inkjet printed circuit since inkjet printed pattern is much thinner than conventional copper foil. Several attempts to make pattern thicker through plating were not successful. Therefore, new sample preparation technique based on adhesive bonding was developed. Fig. 2 shows procedures of peel strength test with new sample preparation. Cu foil with adhesive was attached on 1 cm X 10cm inkjet printed pattern by thermal press. The peel strength was measured according to standard condition of 50mm/min displacement rate and 90° angle.



(a) (b)

(c) (d)

Fig. 2 Procedure of peel strength test: (a) Inkjet printed pattern on substrate (b) Attached Cu plate on Ag pattern, (c) Image of peel strength tester, (d) Image of separated pattern form primer layer on substrate Results and Discussion Thermal properties of primer

As far as properties of primer are concerned, main focus was on the thermal properties since treated substrate was subjected to high thermal stress on sintering of ink. Thermal properties of primer were investigated by DSC and TGA. And glass transition temperature (Tg) and decomposition temperature (Td) were extracted from DSC and TGA data shown in Fig 3 and 4 (a). Tg of primer (118 ℃) was a little lower than that of conventional FR-4 (~130℃). However, Td (360℃) was much higher than conventional FR-4 (~320℃). Therefore, primer is more thermally stable than conventional FR-4. When dried primer was heated at 250 ℃, the highest temperature for sintering of nano Ag ink, there was little change even after 100min as shown in Fig. 4(b), which confirms good thermal stability for inkjet PCB process.

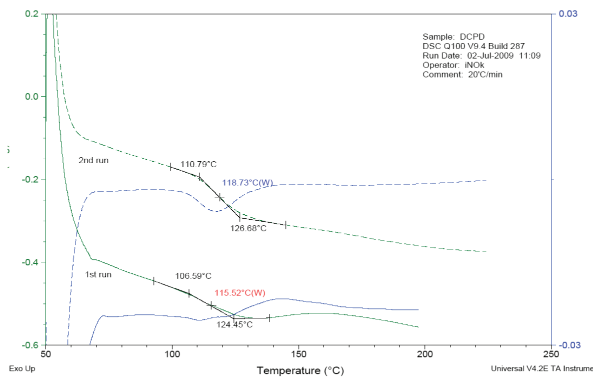
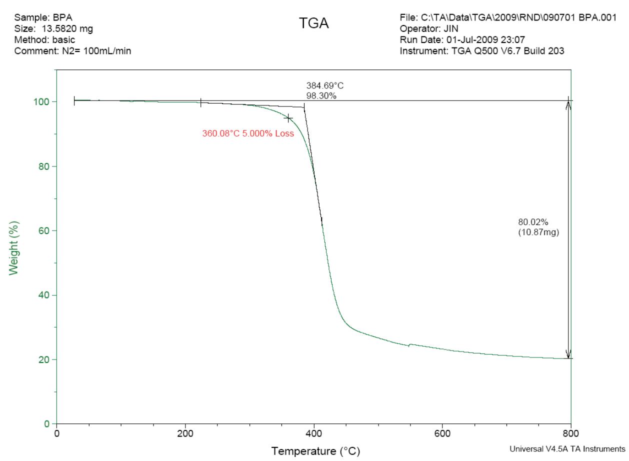
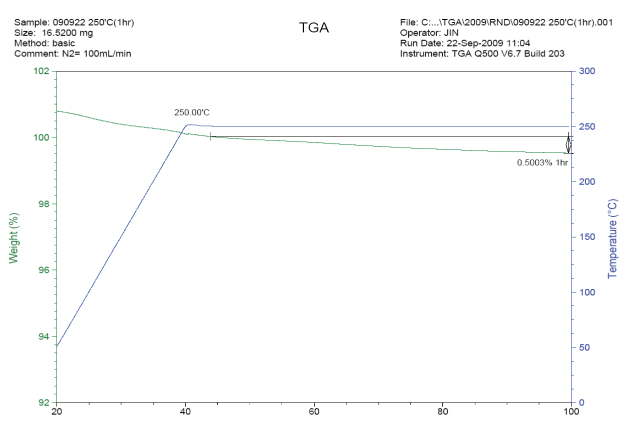


Fig. 3 DSC data



(a)



(b)

Fig. 4 TGA data

Surface Treatment Evaluation

Primer treated substrates were heated for various time at 120℃, which was 5min up to 50min. The contact angle and morphology of 3~5um thick primer layer was analyzed by contact angle analyzer and non contact atomic force microscopy (AFM), respectively. The contact angle between polar nano Ag ink and treated substrate was no less than 50° for 50minutes as shown in Fig. 5. The results demonstrate superior printability of primer treatment substrate, since contact angle is directly related with surface tension between ink and substrate. On the other hand, curing has significant effects on morphology of primer as shown in Fig. 6. In 40min span, 238 nm rough surfaces became 53 nm rough, which is less than a quarter of starting value.

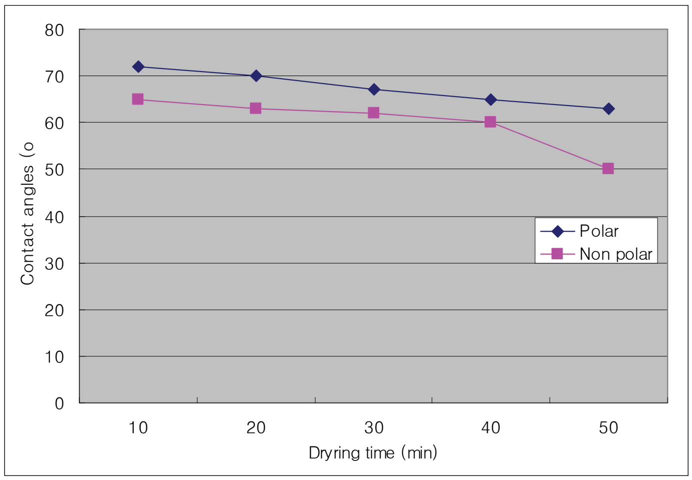


Fig. 5 Contact angles according to treatment time of the primer

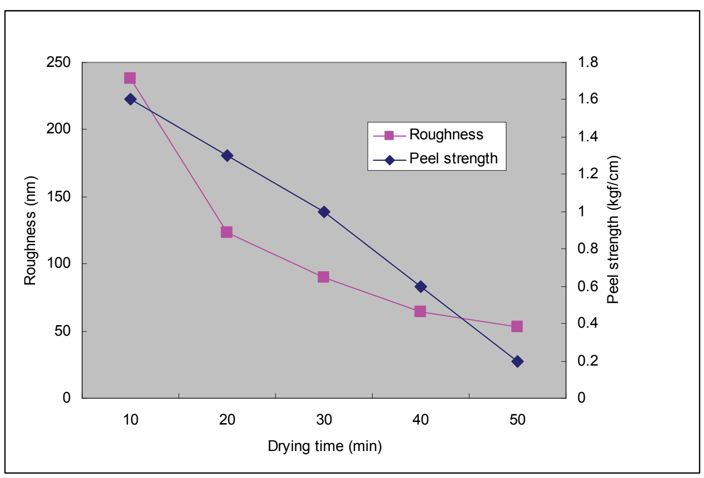


Fig. 6 Related with Roughness and Peel strength according to drying time of the primer

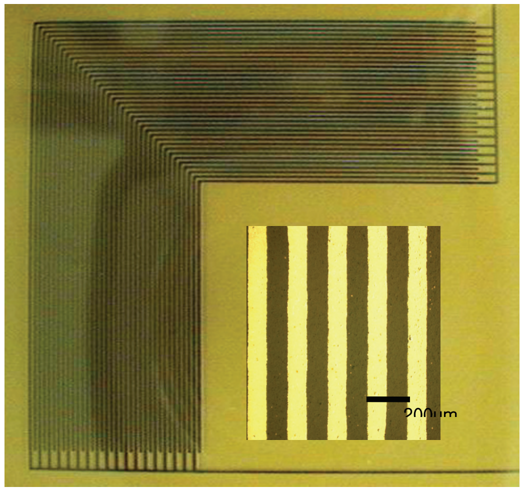


Fig. 7 The inkjet print pattern of 100um/100um

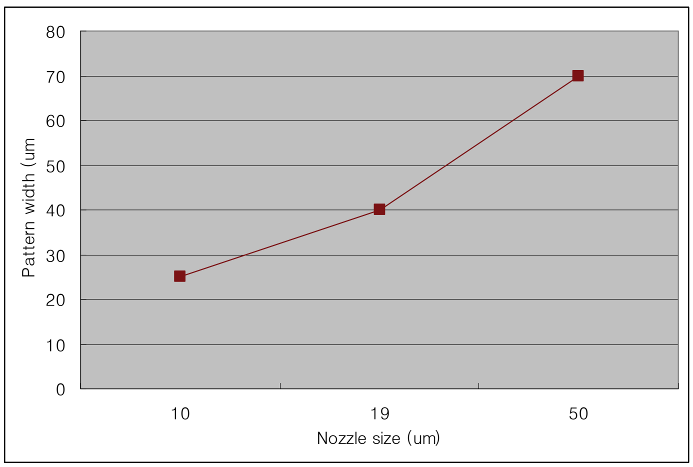


Fig. 8 The width of Ag pattern lines according to Nozzle size

Like contact angle and roughness, peel strength decreases as primer cures. However, it is possible to get 1.5kgf/cm2, which is compatible with conventional FR-4, with some drying. In fact, the adhesion between ink and substrate was very strong in 10 min drying as shown in the Figure.

Even though there were reports saying that peel strength is dependent on either surface roughness or contact angle. it is not clear yet which one is major contributor. Our results suggest peel strength depends heavily on roughness since roughness and peel graphs have same trends. The line definition and edge quality of 100um/100um circuit after sintering was as good as those of conventional circuit as shown in Fig.7. Fine pattern up to 25um/25um was possible using 10um nozzle as shown in Fig 8.

Reliability test of inkjet printed patterns

With inkjet printing, it is possible to have a very fine pattern which is hard to achieve with conventional PCB process. The inkjet printing process is a fully-additive non contacting deposition method, where patterns are formed from digital images. The digital images can be updated and changed during or between the process steps, which offers an extremely flexible manufacturing environment. However, inkjet printed circuit lacks reliability of conventional PCB.

In order to be accepted by conventional PCB industry, the circuit should be as reliable as conventional pattern is. Therefore, the same test vehicle as used for reliability test of conventional PCB was adopted for inkjet printed circuit. Fig. 9 show reliability test coupon composed of inkjet printed circuit and FR-4 substrate.

The series of 100um/100um curvature patterns with substrate treatment were inkjet printed and sintered. The printing quality was compatible with that of conventional PCB as shown on Fig 15.

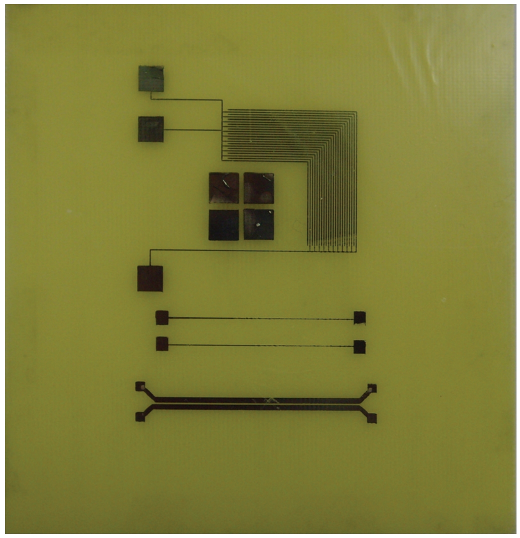


Fig. 9 Inkjet printed patterns for reliability Test

a. Withstanding Voltage Test

A Withstanding Voltage tester is a piece of equipment capable of supplying a range of DC test voltages appropriate for the materials under test with adjustable ramp rate and hold-time settings. Withstanding voltage test is for investigating the effects of the voltage stress of the high voltage and low voltage. Table 1 shows the withstanding voltage test conditions and property. Test coupons have not a shot circuit during withstanding voltages test

Table 1. Withstanding voltage test conditions and property

	Property	Condition of dielectric test
Dielectric Withstanding Voltage	No shot No fire	DC voltage:5000V Measurement time: 30sec Voltage ramping time : 5sec Leakage current : 1mA

b. Anti-migration tests

The metallic ion moving from anode to cathode under fixed voltage at high humidity is called the electrochemical migrations and the most typical migration is called the conductive anodic filament (CAF). CAF is a significant and potentially dangerous source of electrical failure in the PCB and, thus, the overall system of which it is a part. Especially, as PCB’s circuit density gets higher and line and space between patterns become narrower, the CAF resistance becomes much more important among the reliability properties. As shown in table 2, the CAF did not occur even after 100 hours.

Table 2. CAF test data

	Sample 1	Sample 2
Before PCT test	3.62×1012 Ω	3.90×1012Ω
After 24hr (121℃×97%Rh)	1.25×1011Ω	3.01×1012Ω
After 48hr (121℃×97%Rh)	8.21×1010Ω	1.68×1011Ω
After 100hr (121℃×97%Rh)	7.24×1010Ω	8.99×1010Ω

c. Thermal cycling tests (TCT)

TCT test is to investigate the effects of the thermal stress consisted of high temperature and low temperature cycles (air to air). The upper and lower temperature limits for the test were 125℃ and -55℃, respectively. Table 3 shows changes in resistance during the thermal cycles test. The resistance changes of samples were within ± 10% range.

Table 3. TCT test data

	Before test	After test	Change Rate	Test condition
Sample 1	79 Ω	80 Ω	1.0 %	Temp : -55℃/125℃, Cycle : 100cycles Dwell time:15min each
Sample 2	20 Ω	20.5 Ω	3.0 %	
Sample 3	26 Ω	25.1 Ω	- 3.0 %	

Conclusion

In this paper, the capability of the inkjet technology for the Printed circuit board by using novel primer coating technology was discussed. After series of surface treatment experiments with different primers, new treatment has been developed. The primer composed of various resins and hardeners including modified epoxy resins was applied and dried on the substrate before inkjet printing. The surface treatment exhibits wide spectrum of surface morphology upon drying. Surface roughness decrease as drying proceeds. Adhesion between circuit and substrate was more closely related with surface morphology than contact angle. Through proper control of drying time, it was possible to get high quality circuit with good adhesion between circuit and substrate. In fact, peel strength of inkjet printed circuit within 10 min drying was 1.5kgf/cm, which is compatible with that of conventional PCB. The circuit with careful treatment also has high reliability including good thermal stability and anti-migration properties. The width of pattern by using 10um nozzle was obtained 25um.

Acknowledgement

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Tim(Minsu) Lee YoungHoon Kim and YongWook Kim*
Doosan Cooperation, Electro-Materials BG
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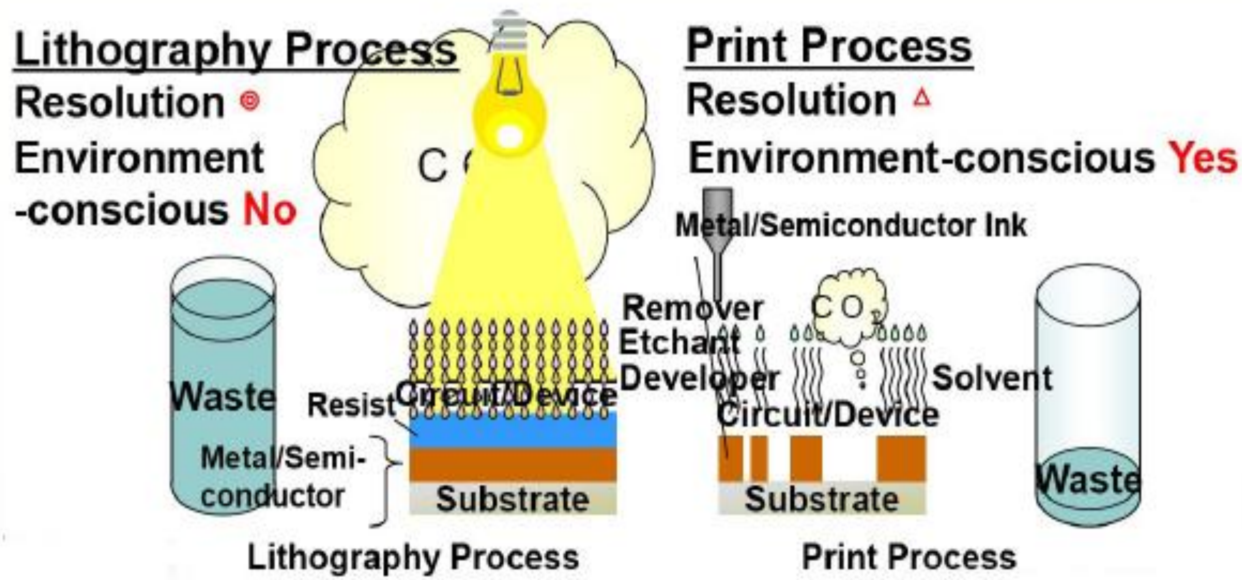
Printed Electronics

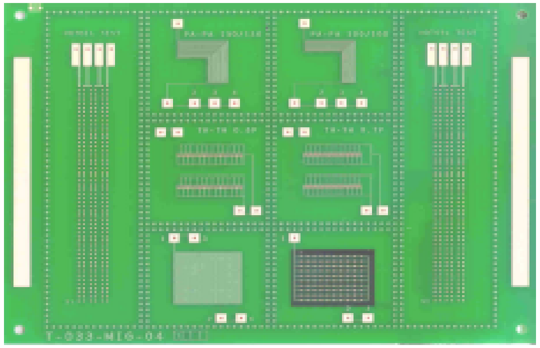
- Electronics produced by printing methods with minimum materials
- Minimize CO2 emission during production process



Important Features of Inkjet Printed Circuit

There are many advantages for inkjet printed circuit technology

Digital printing flexibility
Non-contact
Low materials wastage
Highly accurate deposition
Integration with other processes
Lowest cost manufacturing for many applications



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Problems with inkjet printed circuit

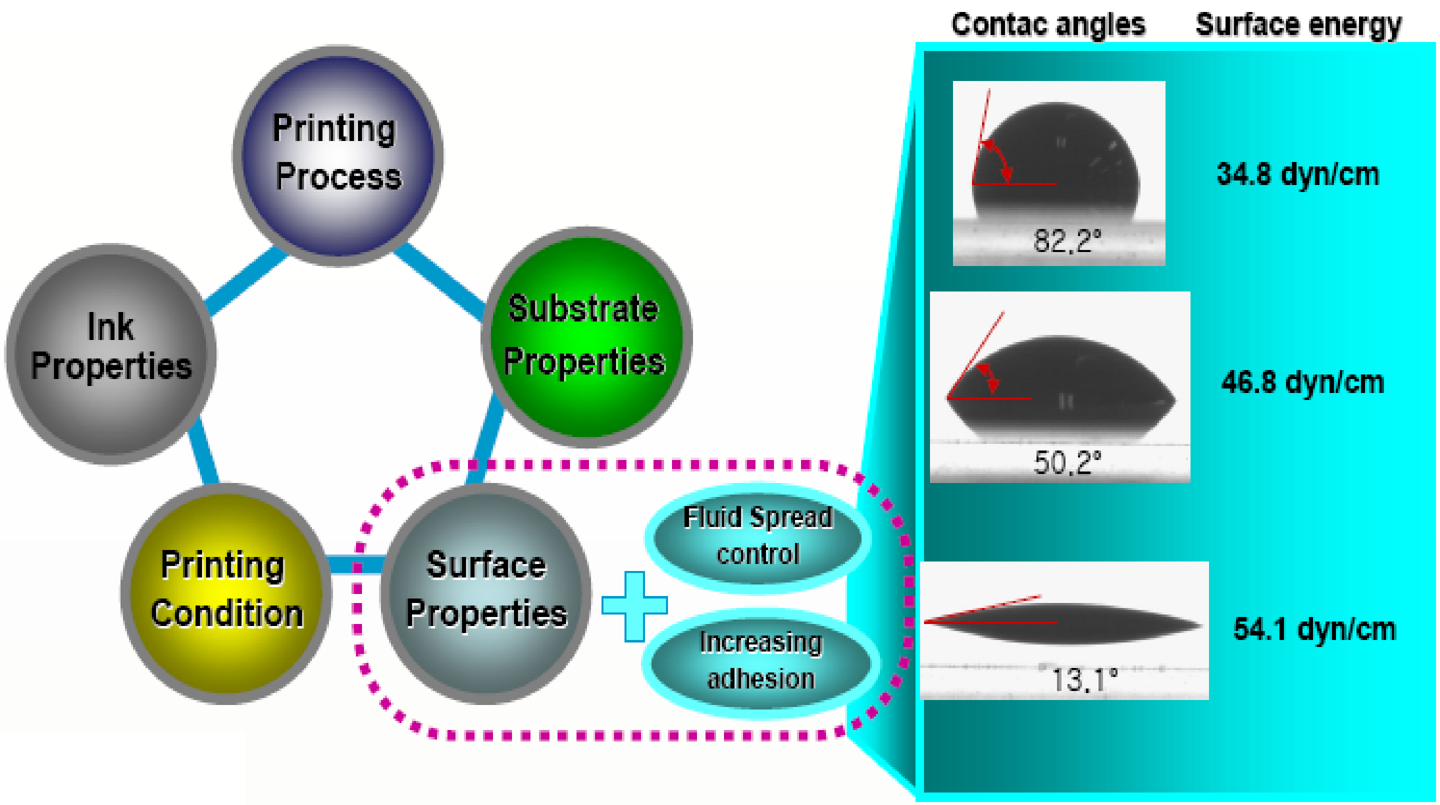
- There are three major problems related with inkjet printed circuit

1. Weak adhesion between circuit and substrate
2. Poor quality and resolution of circuit
3. Low reliability

Hinder the adoption in electronic packaging industry

Solutions

- Efforts are focused more on printer and ink than substrate.
- It is possible to change the pattern quality with surface treatment.



Typical Surface Treatment Methods

- Upon typical treatment, the fine pattern needs heating but does not have enough adhesion for PCB
- Therefore new treatment methods which requires no heating is need for fine pattern and good adhesion

Dry treatment

√ Plasma treatment (CF_4, C_3H_8)
√ Ultraviolet (UV) treatment (O_3, O_2)
√ Corona treatment

Plasma treatment (CF_4) Contact angle : 67° | Room temperature | Plate heating (70℃)

Wet treatment

√ Fluorocarbon coating
√ Fluoro-alkyl-silane coating
√ poly-siloxane coating
√ Surfactant coating

Fluorocaron coating Contact angle : 95° | Room temperature | Plate heating (70℃)

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Characteristics of New Materials

Print of high quality and resolution

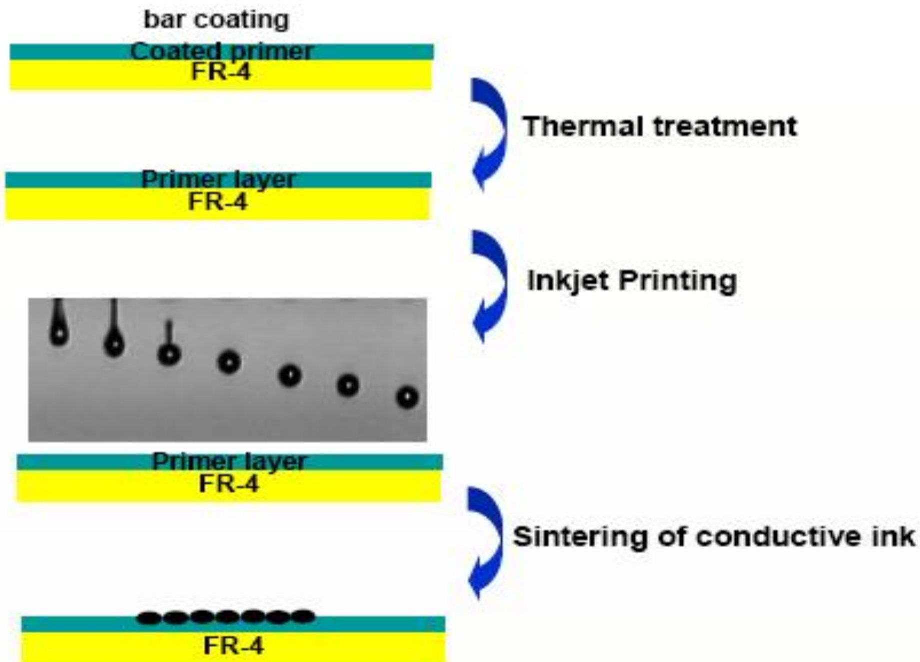
- Contact angles up to 70°
- Preventing the phenomenon of merging of deposited droplets
- Printing process at room-temperature

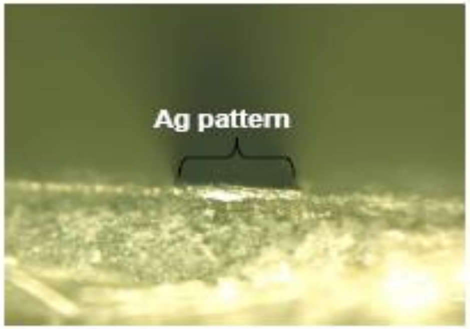
Must Have Both Properties → New Treatment Material

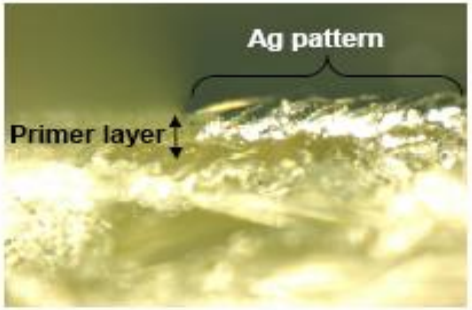
Adhesion between pattern and substrate

- Peel strength up to 1kgf/cm^2
- Outstanding Coating properties
- Materials with good thermal stability

Surface treatment system







Resins system of primer

Multifunctional epoxy resin
+
Aromatic resin

+

HARDENER
- Aromatic amine
- Anhydride
- DICY

+

ADDITIVE
- Leveling Additive
- Filler etc.

- Good coating properties as well as high thermal resistance are required
- Epoxy resin based system can satisfy all requirements

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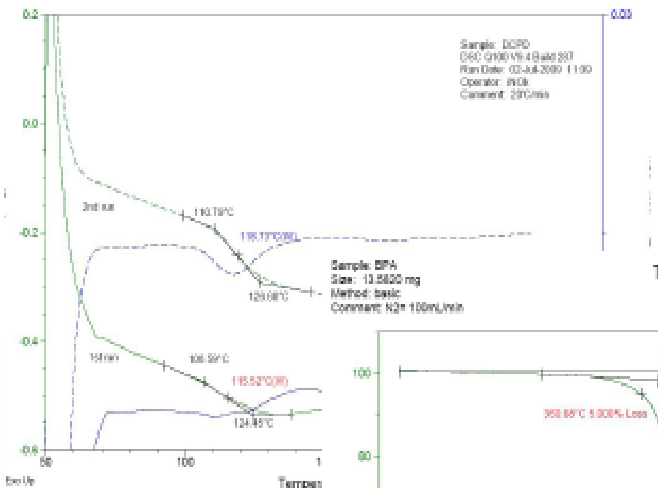
- ◇ Overview
- ◇ Development of Primer for Inkjet Printed Circuit
  - √ Background of Development
  - √ Strategy of Primer system
  - √ New Resin System
- ◇ **Characteristics of Inkjet Printed Circuit with Surface Treatment**
  - √ **Thermal Properties**
  - √ **Surface Properties**
  - √ **Peel Strength Properties**
  - √ **Flexibility Properties**
- ◇ Reliability of Inkjet Printed Circuit
- ◇ Conclusion

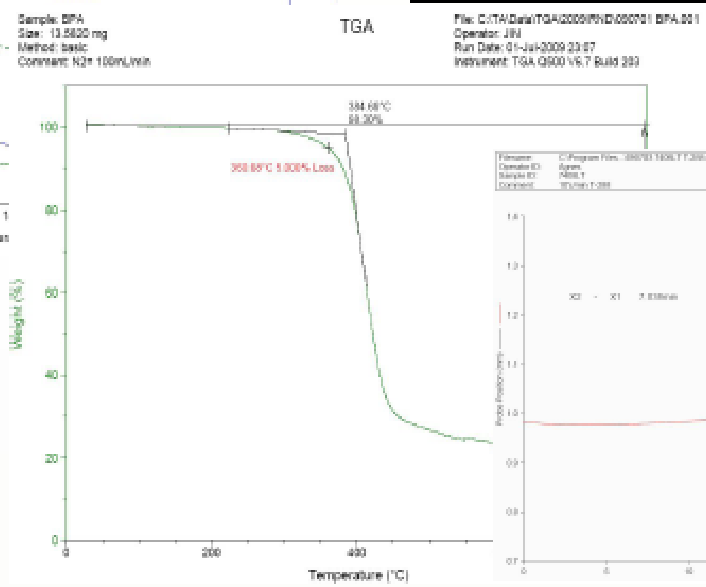
Thermal properties-1

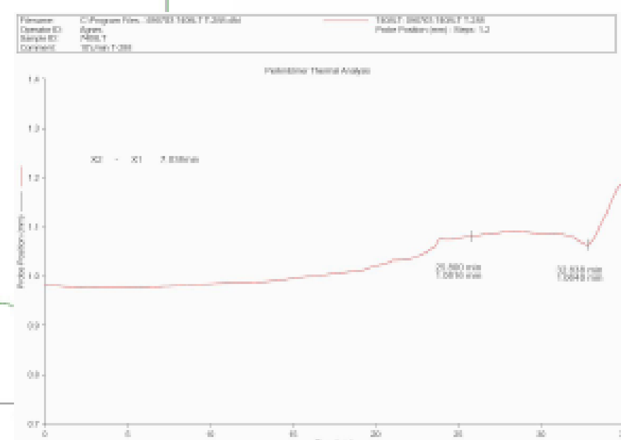
The cured primer has good thermal properties with high Tg and Td



Item	Properties
DSC Tg	118 ℃
T-260	60min
T-288	20min
Td (5% Loss)	360 ℃

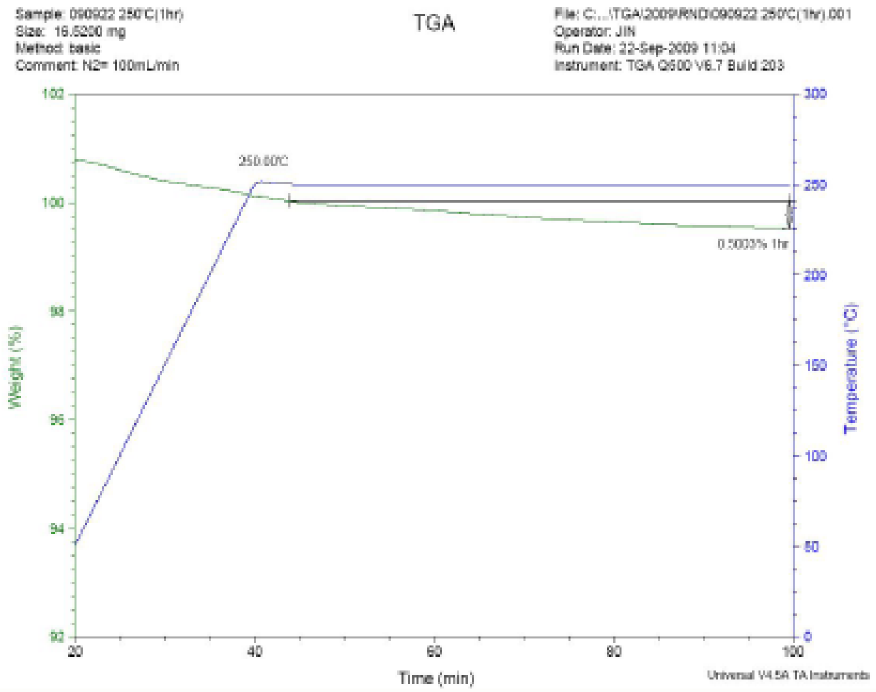
TGA





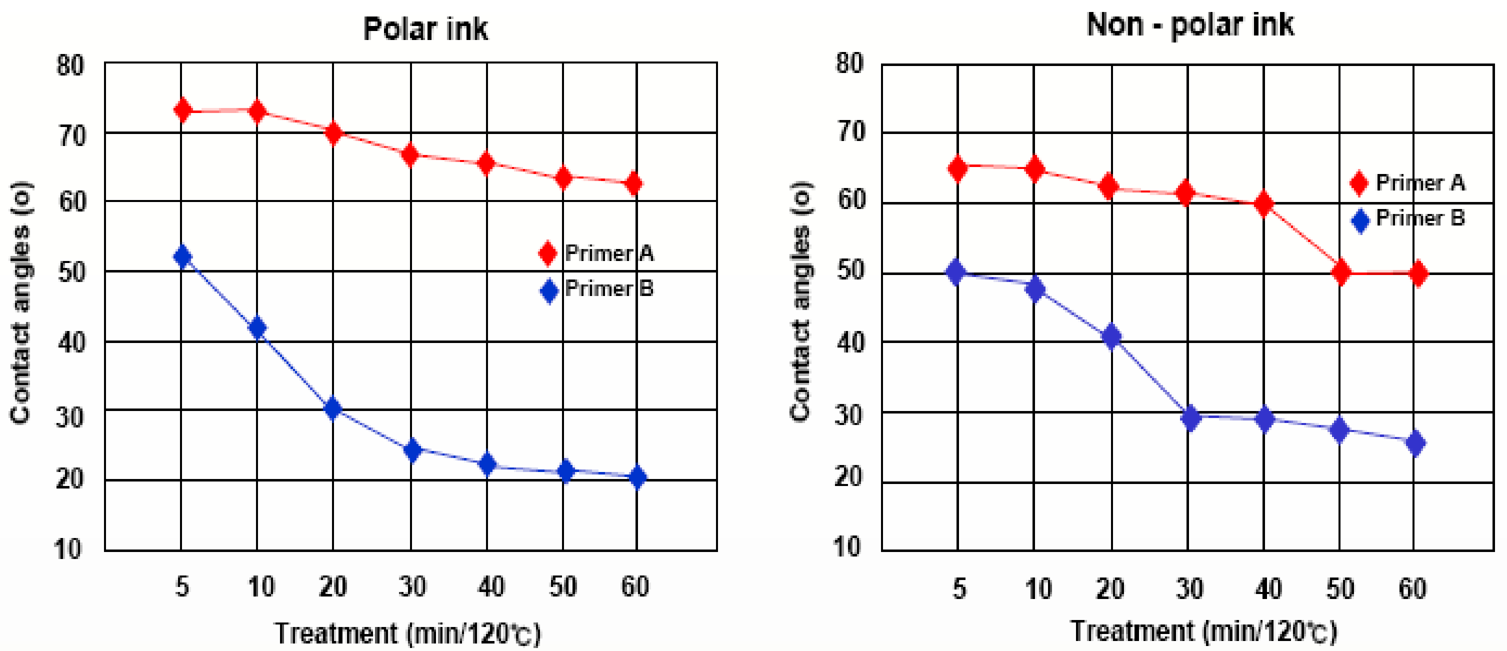
Thermal properties-2

- After 60min sintering at 250℃, the weigh loss is only 0.5% which shows good inkjet printing processing



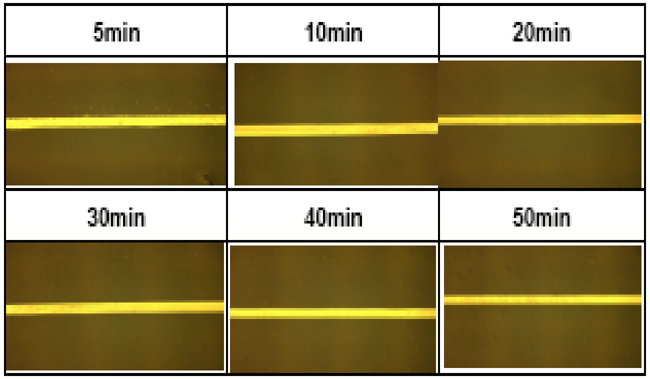
Contact angles according to hardener and ink polarity

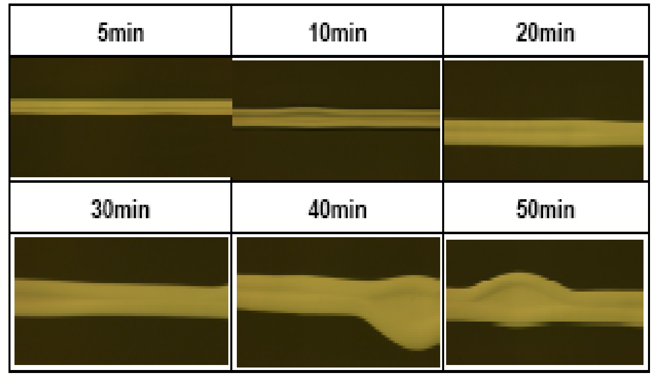
Contact angles decreased as the treatment progressed, regardless of polarity of ink and primer type

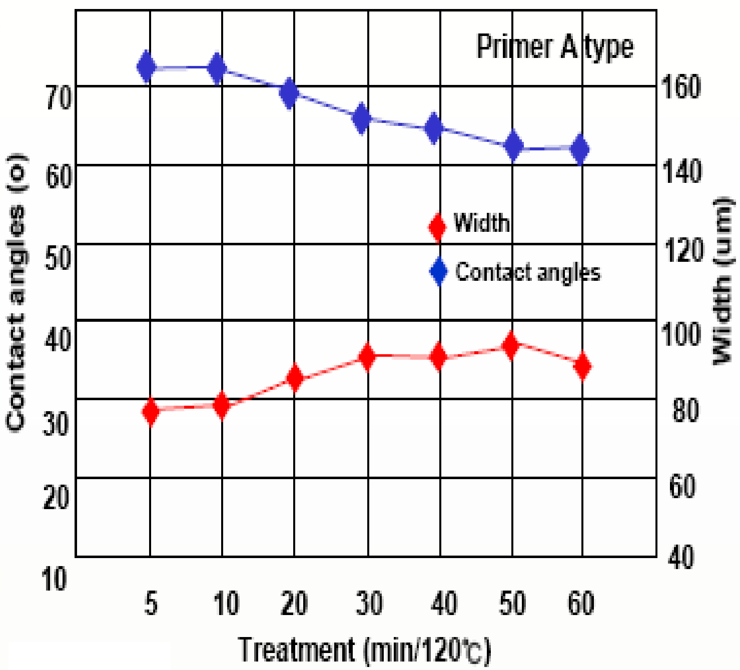


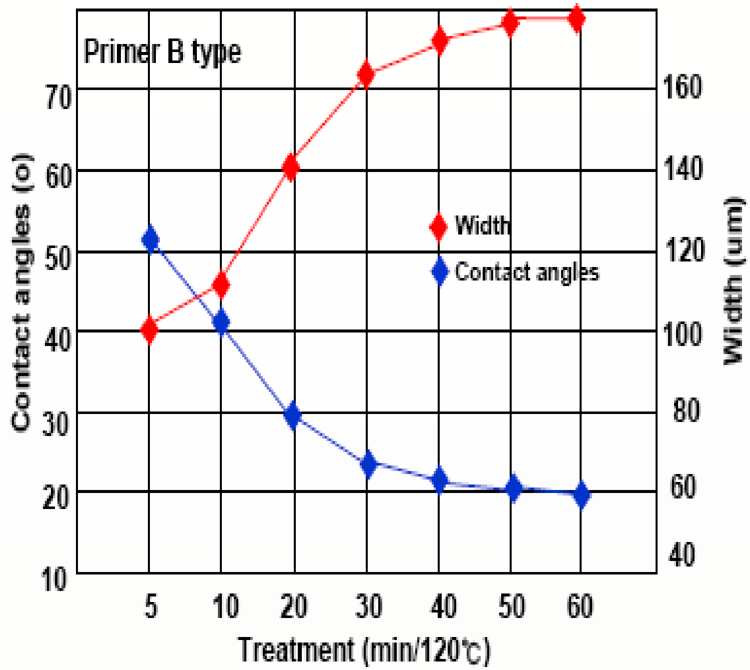
Polar ink dissolved in tri-ethylene glycol mono-ethyl ether (35.9dyne/cm)
Non-polar ink dissolved in n-Tetradecane (29.1dyne/cm)

Contact angles, pattern width and printing quality



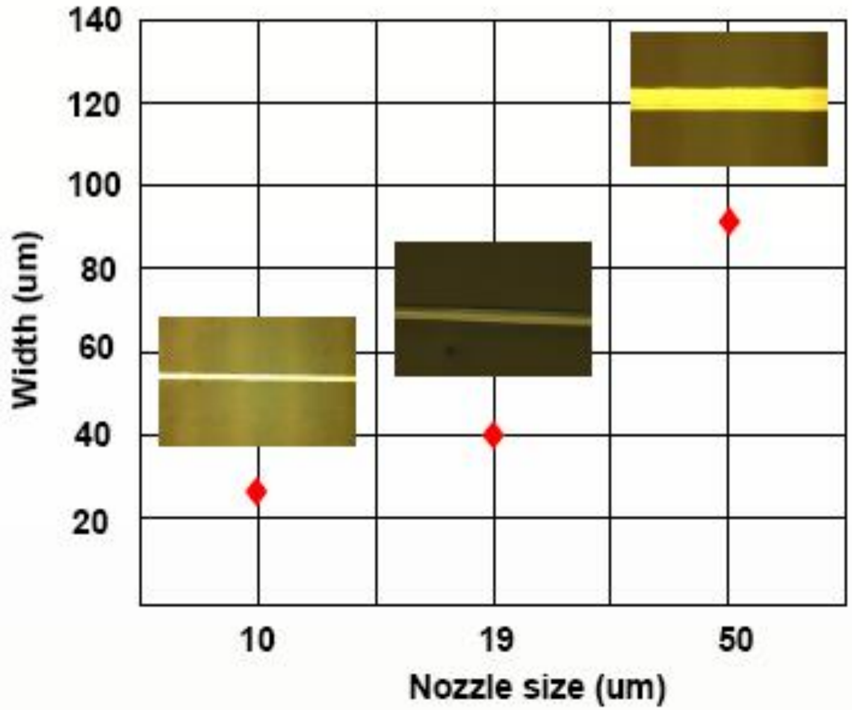






Pattern width according to nozzle size

- Fine pattern up to 25um/25um was possible using 10um nozzle .



Peel strength test with new sample preparation technique

Ag pattern on substrate

Ag ink of concentration with 35 wt% was used
Dimension of a rectangular pad shape was 1 cm by 10cm.
Annealing for 30minutes at 150℃

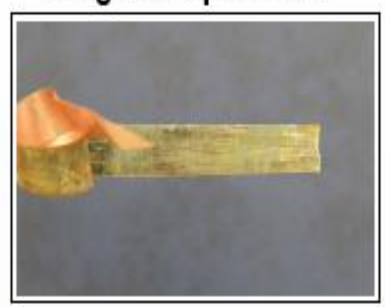
Attached Cu foil on inkjeted pattern

Cu foil with adhesion was attached
on inkjeted pattern by thermal press

Image of peel strength instrument

The adhesion was measured by peel strength tester
at 50mm/min. (angle is up to 90˚)

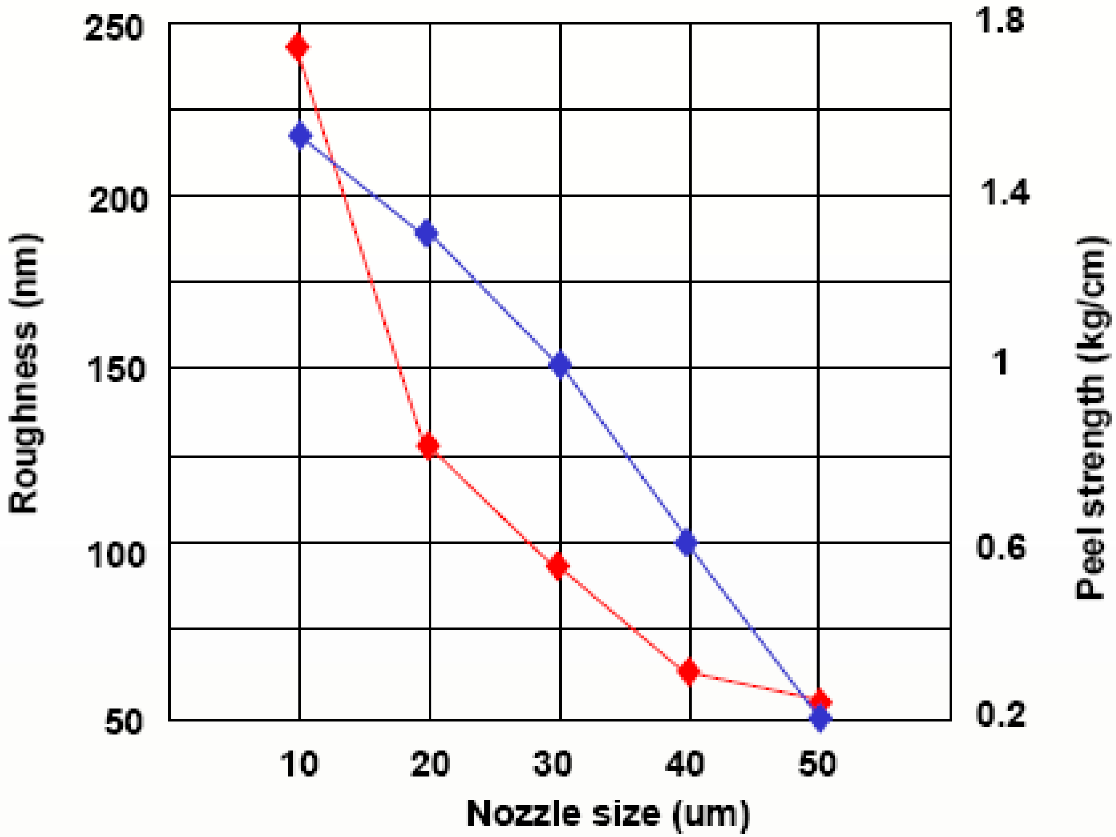
Image after peel test



Peel strength : 1 ~ 1.5 kgf/cm^2

Effects of drying on surface roughness

- Curing has significant effects on surface morphology of treated substrate.
- It is possible to have very strong adhesion between Ag pattern and substrate with proper drying



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Inkjet printing system

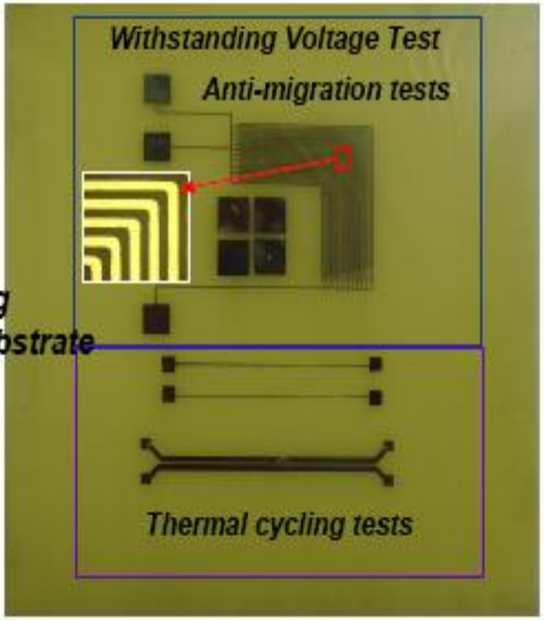
Image of KITECH Micro system team Lab

◇ Single nozzle inkjet system

- Microfab. single nozzle
- Nozzle diameter: 50 μm
- 2-axis stage: 200mm x 200mm
- CCD Camera & LED backlight

Inkjet printing on primer substrate

Test coupon



Reliability properties

Anti-migration test

	Sample 1	Sample 2
Before test	3.62×10^{12} Ω	3.90×10^{12} Ω
After 24hr (121℃×97%Rh)	1.25×10^{11} Ω	3.01×10^{12} Ω
After 48hr (121℃×97%Rh)	8.21×10^{10} Ω	1.68×10^{11} Ω
After 100hr (121℃×97%Rh)	7.24×10^{10} Ω	8.99×10^{10} Ω

Withstanding voltage test

Property	Condition of dielectric test
No short No flame	DC voltage:5000V Measurement time: 30sec Voltage ramping time : 5sec Leakage current : 1mA

Thermal cycling test

	Before test	After test	Change rate	Condition of thermal cycling test
Type A	79 Ω	80 Ω	1.0 %	◇ Procedure - Temperature : - 55℃ ~ 125℃ - Step : 30 min - Measurement time : 100 cycle
Type B	20 Ω	20.5 Ω	3.0 %	
Type B	26 Ω	25.1 Ω	- 3.0 %	

Conclusion

- New primer with good thermal and coating properties was developed.
- Surface roughness of treated substrate decrease as curing proceeds.
- Inkjet printed pattern quality is inversely related to the contact angle.
- It is possible to get high quality inkjet pattern with strong adhesion upon proper drying of primer.
- The inkjet printed circuit with careful treatment has high reliability including good thermal stability and anti-migration properties.