# A Study of Digital Fabrication using High-resolution Liquid Toner Electrophotography

Atsuko lida, Koichi Ishii, Yasushi Shinjo, Hitoshi Yagi, Mitsunaga Saito, Hideki Nukada, Masaki Takahashi, and Masahiro Hosoya, Corporate Research & Development Center, Toshiba Corporation, Kawasaki, Japan; Naoko Yamaguchi, Semiconductor Company, Toshiba Corporation, Kawasaki, Japan

#### Abstract

We have studied a new digital fabrication technology using highresolution liquid toner electrophotography, which consists of fine liquid toner, high-resolution exposure unit and non-electrical transfer. Fine pitch multi-line patterns of Cu wiring can be obtained by printing fine lines with seed toners, and by electroless plating deposited on lines. Seed toners are submicrons in diameter with superfine conductive particles on the surface. The multi-line patterns of 1 pixel line-width (21.6 micrometers) with the volume resistivity of  $2.1 \times 10^6 \Omega \cdot cm$  were realized by using a liquid toner developing process with a 1200 dpi resolution LED.

Furthermore, the capability of high-resolution multi-line pattern formation has been investigated by theoretical analysis. Liquid toner developing process with a 2540 dpi resolution LSU was examined by numerical simulations, taking account of the potential distributions of multi-line patterns. The capability of multi-line pattern formation of Line and Space (L/S) = 10/10 micrometers was indicated and the experimental result confirmed it.

#### Introduction

Fine pitch pattern formation of wiring circuit boards and reduction in the cost of manufacturing processes are critically important requirements for electronic components and semiconductor packages. Recently, digital fabrication of electronic components using printing technology has been reported.<sup>14</sup> Digital fabrication of wiring circuit boards offers several advantages, for example mask-less process and simple process, and reduced costs.

We have been developing a high-resolution liquid toner electrophotographic imaging technology, with the potential to produce fine images equal in quality to those produced by offset printing. <sup>5-14</sup> Extremely, high-resolution images have been realized by our technology which includes full color Image-On-Image (IOI) developing process, high-resolution Laser Scanning Unit (LSU) with 2540 dpi, and non-electric transfer process calling "Shearing transfer".<sup>8,9</sup>

This paper reports on a study of a new digital fabrication process using liquid toner electrophotography. The fabrication process shown in Figure 1 is as follows: firstly, fine pitch patterns are formed on the substrate by using seed toners, and then conductive layers are deposited on it by electroless plating. Seed toners were prepared by coating their surface with superfine conductive particles. Compared with electrophotographic systems using dry toners,<sup>1,2</sup> it is possible to achieve higher resolution patterns because of edge sharpness, and to provide higher performance in electroless plating because of uniform dispersion of conductive particles over the formed line surface. The patterns can be transferred on the substrate, which is almost or partly covered with metallic layers, by using shearing transfer.



Figure 1. New process of fine pitch pattern formation using liquid toner electrophotography technology.

In our previous paper, we had analyzed the high-resolution liquid toner developing process of very fine single dot at 2540 dpi resolution, theoretically and experimentally.<sup>10.14</sup> In the present study, the developing process of multi-line patterns was analyzed to clarify the capability of high-resolution multi-line pattern formation. The developing process taking account of the potential distributions of latent images formed with the 2540 dpi resolution LSU was examined using numerical simulations, based on the electrophoretic characteristics of liquid toner and on the electrostatic forces.

## **Process of Fine Pitch Pattern Formation**

Fine pitch pattern formation consists of two main processes. Firstly, images of fine pitch pattern are printed on a substrate by using seed toners, and then conductive layers are deposited on it by electroless plating.

#### Image Formation of Fine Pitch Pattern Lines

The configuration of our liquid toner electrophotographic system is shown in Fig. 1. The system includes a photoreceptor drum, a scorotron charger, LED with a resolution of 1200 dpi, a development unit, a dryer, and a transfer unit at the periphery of the photoreceptor drum. The toner image is dried on the photoreceptor and transferred to the intermediate transfer roller by shearing transfer, and then secondary transferred to and fixed on a substrate. Silicon wafers, glass, and resin films such as polyimide, grass-epoxy, or polyethylene terephthalate were used for the substrate.

The seed toner was based on the toner developed for our image formation and the average diameter was 0.2 micrometer. Seed toners were prepared by coating their surface superfine conductive particles. The superfine conductive particles were metal particles of Ag, Cu, Pd, and any other materials with catalytic ability for seed of electroless plating.

The fine pitch pattern printed by our liquid toner electrophotographic system is shown in Fig. 2. The L/S = 1pixel/1pixel was formed on silicon wafer which was laminated with dry-film of epoxy resin to be insulating layer. The fine pitch pattern formed on the photoreceptor surface was transferred to the substrate without deterioration during our transfer process.



Figure 2. Fine pitch pattern of L/S = 1pixel/1pixel using seed toner printed by liquid toner electrophotography.

#### Surface Modification After Printing Pattern

Surface modification was applied on the patterns after printing, in order to enhance the adhesion of interface between the pattern surface and the metal layer deposited by electroless plating. The pattern surface after adding  $O_2$  gas plasma showed slightly rough surface and the adhesion between the printed pattern and Cu layer was dramatically increased.

## **Electroless Plating Proces**

Samples were dipped in low concentration acid after cleaning process. Then, Cu layer was deposited on printed pattern by using a plating solution based on ethylenediamine-tetraacetic acid.

The Scanning Electron Microscope (SEM) image of Cu conductive pattern of L/S = 1pixel/1pixel is shown in Fig. 3. The thickness of Cu layer was about 4 micrometers. The adhesion of interface between seed toner layer and Cu layer was kept sufficient to overcome the stress included in Cu layer. The SEM image of Fig. 4 shows an edge of Cu conductive line. The edge sharpness of Cu conductive lines was less than 2 micrometers. The high-resolution multi-line pattern was obtained by using liquid toner electrophotography.



Figure 3. The SEM image of Cu conductive pattern of 4 micrometers thickness deposited by electroless plating.



Figure 4. The SEM image of edge of Cu conductive line.

The volume resistivity of Cu conductive line was  $2.1 \times 10^{6} \Omega \cdot cm$ , which is 1.2 times that of bulk Cu. Since the volume resistivity was slightly higher than that of bulk Cu, the fabrication processes were not sufficiently optimized in the present study. That is an issue to be tackled in the next phase of this research.

The change of resistance of wiring patterns of L/S = 2pixels/4pixels shown in Fig. 6 was measured after applying the reflow condition of 260 °C at peak temperature. Samples were covered with Ni/Au layers by adding the electroless plating. The resistance values were stable after the reflow process.



Figure 5. Wiring patterns for measuring the resistance.

## Theoretical Analysis of Capability of Multi-line Pattern Formation using Liquid Development

The capability of multi-line pattern formation was examined using liquid development with 2540 dpi resolution LSU system. The numerical analysis was based on the two-dimensional continuity equations and Poisson's equation taking into account the charges of the toner particles and the counter ions, which are positively and negatively charged, respectively. The calculation was performed using differential equations.<sup>13-17</sup>

#### Two-Dimensional Liquid Development Model

The model analyzed is a multi-line pattern including 10 lines, whose line width is 10 micrometers and space is 10, 20 and 30

micrometers in each case. The calculated surface potential distributions Vp for L/S = 10/10, 10/20 micrometers are as shown in Fig. 6. Surface potential of multi-line pattern of L/S = 10/10 micrometers was lower because of the narrow space.



Figure 6. Potential distribution of multi-line of L/S = 10/10, 10/20 micrometers, respectively (V0 = 700 V).

In the initial state of the development, both the charge densities,  $\rho_p$  and  $\rho_n$  are homogeneous in the area of analysis and their absolute values are the same,  $P_0 = -P_0$ . The space and time distributions of the charge density are brought about by the continuity equations (1, 2) and Poisson's equation (3). The values used in the analysis are listed in Table 1.

$$\frac{\partial \rho_p}{\partial t} = -\frac{\partial (\mu_p \rho_p E_x)}{\partial x} - \frac{\partial (\mu_p \rho_p E_y)}{\partial y}$$
(1)

$$\frac{\partial \rho_n}{\partial t} = + \frac{\partial (\mu_n \rho_n E_x)}{\partial x} + \frac{\partial (\mu_n \rho_n E_y)}{\partial y}$$
$$\frac{\partial^2 \phi_i}{\partial x^2} + \frac{\partial^2 \phi_i}{\partial y^2} = -\left(\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y}\right) = -\frac{(\rho_p + \rho_n)}{\varepsilon_i}$$
(2)

Table 1: Parameters for the Numerical Simulation

Prameters	Symbol	Value	Unit
Development time	Td	48	msec
Development nip	Wd	5	mm
Initial charge density of liquid toner	P <sub>0</sub>	1.54	C/m3
Relative dielectric constant of liquid toner	8t	2.03	-
Development gap	dt	150	μm
Mobility of liquid toner	μ <sub>p</sub>	4.00E-10	m2/V*sec
Mobility of counter ion	μn	2.00E-10	m2/V*sec

#### The Potential and Charge Density Distribution of Multi-line Pattern

The result indicates that the potential gradient in the positive direction of y-axis is low except in the vicinity of the photoreceptor. The electric field is rather small in the major part of the developing gap. Time-dependence toner distribution of L/S = 10/10 micrometers is shown in Fig. 7. Clear contrast of the charge density was observed in the vicinity of the photoreceptor. The toner particles migrate toward the image area, whereas they migrate away from the non-image area. On the other hand, in the

vicinity of the development roller, the density of the toner particles becomes low due to the effect of the low potential gradient mentioned above. In the middle of the developing gap, the charge density is almost unchanged.



Figure 7. Time-dependence toner distribution of multi-line of L/S = 10/10 micrometers in development gap (Vb = 400V).

#### **Multi-line Formation**

Figure 8 shows the L/S-dependence deposition of multi-lines of L/S = 10/10, 10/20 micrometers. The edge effect was observed in Fig. 8, which is a trend such that both edge lines in multi-line pattern become narrower than those of inside lines. In particular, the edge effect is rather significant for fine pitch mode. Image processing will be required for high-resolution multi-line pattern formation.



Figure 8. Line/Space-dependence toner deposition of multi-line of L/S = 10/10, 10/20 micrometers.

#### Toner Image by Developing with 2540 dpi LSU

Toner image by developing liquid toner with 2540 dpi resolution LSU system is shown in Fig. 9. Figure 9 shows the brightness for each line of L/S = 1pixel/1pixel (1pixel = 10 micrometers) multiline formed on the paper. The edge effect is observed in Fig. 9; the brightness of edge line was lower than that of other lines.



Figure 9. Experimental result using 2540 dpi LSU; brightness for each line of the L/S = 1 pixel/1 pixel multi-line formed on the paper.

## Conclusion

Fine pitch multi-line patterns were obtained by liquid toner electrophotography technology. The multi-line pattern of L/S = 1pixel/1pixel, was formed by printing the seed toner in 1200 dpi resolution LED, and Cu layer was deposited on the printed lines by electroless plating. The resistivity of Cu conductive lines was  $2.1 \times 10^{-6} \Omega \cdot cm$ , and the resistance values were stable in the case that reflow process was applied.

The liquid toner developing process for multi-line patterns was theoretically analyzed with 2540 dpi resolution LSU. Although the surface potential of latent image for L/S = 10/10 micrometers becomes lower because of the narrow space, the multi-line patterns formed on the photoreceptor are sufficiently isolated from one another. Edge effect is observed for fine pitch multi-line pattern. The multi-line of L/S = 1pixel/1pixel was formed by liquid toner with actual 2540 dpi resolution LSU system. The numerical analysis of fine pitch multi-line patterns agrees well with that of the actual toner images experimentally obtained.

The results confirm that the fabrication process using liquid toner electrophotography is available to form high- resolution multi-line patterns.

#### Acknowledgments

The authors wish to thank to Dr. T. Yasumoto and Ms. N. Yanase, Semiconductor Company, Toshiba Corporation, for advice on the surface modification. They are grateful to Mr. S. Sakamoto and Ms. M. Umehira, C. Uyemura & Co., Ltd., for supporting the electroless plating process.

## References

- 1. Yamaguchi, et al., Japan Hardcopy 2004, p.121 (2004).
- 2. H. Aoki, et al., Proceedings of IS&T's NIP20, p.241 (2004).
- 3. P. Calvert, et al., Chem. Mater. 2001, vol.13, p3299
- 4. P. H. Kydd, et al., Proceedings of IS&T's NIP14, p.222 (1998).
- 5. M. Hosoya, et al., Japan Hardcopy 2000, p.161 (2000).
- 6. H. Yagi, et al., Proceedings of IS&T's NIP16, p.246 (2000).
- M. Hosoya, et al., International Congress of Imaging Science (ICIS'02), p.592 (2002).
- 8. S. Hirahara, et al., Japan Hardcopy2001 Fall Meeting, p.64. (2001).
- A. Iida, et al., International Congress of Imaging Science (ICIS'02), p.596 (2002).
- 10. H. Yagi, et al., Japan Hardcopy 2003 p. 281 (2003).
- 11. M. Takahashi, et al., Japan Hardcopy 2003 p. 13 (2003).
- 12. K. Ishii, et al., Proceedings of IS&T's NIP19, p.9 (2003).
- 13. I. Takasu, et al., Proceedings of IS&T's NIP20, p.1027 (2004).
- 14. Y. Shinjo, et al., Japan Hardcopy 2004 p. 31 (2004).
- 15. I. Chen, J. Imaging. Sci. and Technol., 39 (6), p.473 (1995).
- 16. Y. Kishi, et al., Japan Hardcopy 1999 p.177 (1999).
- 17. F. J. Wang, et al., Proceedings of IS&T's NIP15, p.623 (1999).

## **Author Biography**

Atsuko Iida received B.S. and M.S. degrees in applied physics from Science University of Tokyo, Tokyo, Japan in 1981 and 1983, respectively. Since 1983 she has been with the Corporate Research & Development Center, Toshiba Corporation, Kawasaki, Japan, where she is engaged in the development of the electrophotography process. She is a member of The Japanese Society of Printing Science and Technology.