INTERNATIONAL JOURNAL OF PRECISION ENGINEERING AND MANUFACTURING Vol. 16, No. 11, pp. 2347-2352 OCTOBER 2015 / 2347
DOI: 10.1007/s12541-015-0302-z ISSN 2234-7593 (Print) / ISSN 2005-4602 (Online)

Reverse Offset Printing of Transparent Metal Mesh Electrodes using an Imprinted Disposable Cliché

Young-Man Choi[1], Jeongdai Jo[1], Eonseok Lee[1], Yunseok Jang[1], Inyoung Kim[1], Jae Hong Park[2], Chung-Mo Yang[2], Woo Choong Kim[2], Taik-Min Lee[1], and Sin Kwon[1,#]

1 Department of Printed Electronics, Korea Institute of Machinery and Materials, 156 Gajeongbuk-ro, Yuseong-gu, Daejeon, 34103, South Korea
2 Nanostrucutures R&D Team, Korea National Nanofab Center, 291 Daehak-ro, Yuseong-gu, Daejeon, 34141, South Korea
Corresponding Author / E-mail: skwon@kimm.re.kr, TEL: +82-42-868-7219, FAX: +82-42-868-7176

KEYWORDS: Reverse offset printing, Metal mesh, High-precision patterning, Transparent electrodes

The clichés used in reverse offset printing are typically fabricated using photolithography and etching processes applied to a Si wafer or glass substrate. Because those fabrication processes make clichés cost high, they are cleaned and reused in repeated printing processes. The cleaning process tends to reduce the quality and throughput of reverse offset printing techniques. This paper describes reverse offset printing using a noble disposable cliché. Disposable clichés may be used once or a few times, and then they may be discarded. They are fabricated by imprinting methods applied to an ultraviolet curable resin on a flexible plastic film. The high adhesion of the plastic film facilitates patterning on the disposable clichés and yields patterns similar to those achieved using hard clichés. The disposable clichés and roll-to-plate reverse offset printing methods were used to fabricate highly transparent conductive electrodes consisting of metal meshes with a linewidth of 3.6 μm. The transmittance of the metal mesh electrodes was 98% and the sheet resistance was 80 Ω/□.

Manuscript received: May 29, 2015 / Revised: August 5, 2015 / Accepted: August 6, 2015

1. Introduction

The field of printed electronic device manufacturing has seen the rise of a new paradigm over the last decade. Conventional and modified printing techniques have been developed to replace photolithography processes. The new printing techniques have only shown success in limited applications to relatively large patterns, such as electrodes for use in solar cells,[1] multi-layer ceramic capacitors,[2] and radio-frequency identification tags.[3] Among the many printing methods developed thus far, reverse offset printing yields a comparably high resolution, down to the sub-micrometer level.[4] The high-precision patterning properties of this method render it useful for fabricating thin film transistors (TFTs)[5-9] and touch screen sensors.[10] Chang et al.[5] printed source/drain patterns characterized by L/S=30/7 μm using a photoresist ink for thin film transistor arrays. The authors also reported the fabrication of a reverse offset-printed touch screen sensor with a linewidth of 10 μm[10] and the mechanism of the transfer printing.[11] Recently, Kusaka et al.[9] demonstrated the preparation of a fully printed TFT using a wet-on-wet printing process, yielding L/S=1/1 μm. The main obstacle to commercializing reverse offset printing is productivity. Several factors have kept the productivity at low levels. One such factor is the need for cliché cleaning. After each printing cycle, the clichés must be cleaned to remove remnant ink prior to the subsequent printing process. Cleaning increases the process time and requires significant quantities of cleaning solution. The use of cleaning processes limits the implementation of roll-to-roll reverse offset printing processes. Another factor that hinders reverse offset printing productivity is the difficulties associated with remnant ink recycling. Most functional inks used in printed electronics, such as silver nanoparticle inks, are expensive. The ink left on a cliché should ideally be collected for recycling. Recycling also requires additional time and components. To overcome these issues, we propose the implementation of a disposable cliché technology. Imprinting methods using an ultraviolet curable resin, so-called UV imprinting, have been used to prepare nano-scale features at economical prices.[12-15] This method enables the continuous duplication of clichés without limit. After use, the clichés may be disposed of or rolled without cleaning into a recycling post-process. A continuous supply of flexible clichés makes roll-to-roll reverse offset printing possible. In this paper, we present a modified reverse offset printing using an imprinted disposable cliché. Highly defined pattern and high surface

© KSPE and Springer 2015

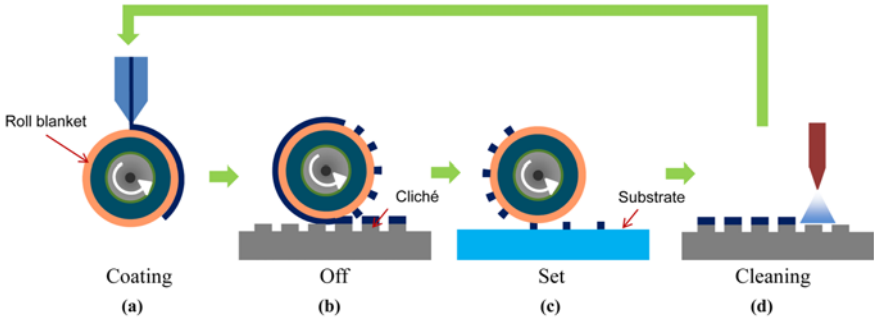


Fig. 1 Continuous reverse offset printing process: (a) an ink film was coated onto the blanket roll; (b) the ink film was patterned using a cliché; (c) the pattern was transferred onto a substrate; (d) the cliché was cleaned. This process was then repeated during continuous printing

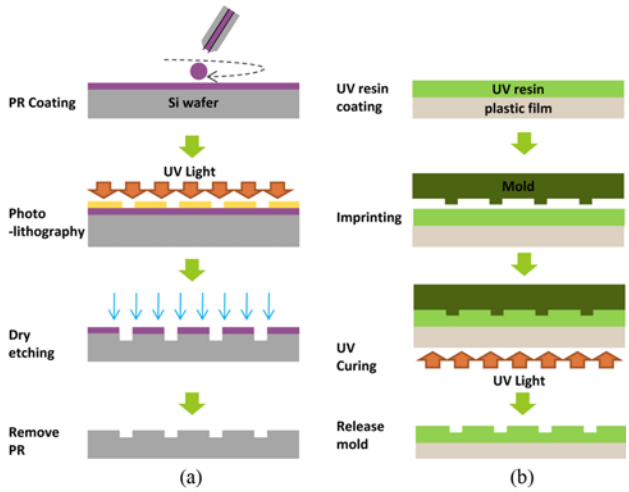


Fig. 2 Cliché fabrication methods: (a) conventional clichés (hard clichés); (b) disposable clichés (soft cliché)

energy of the disposable clichés enables to replace hard clichés. We successfully demonstrated to fabricate transparent conductive electrodes (TCEs) using the proposed process.

2. Methods

Fig. 1 demonstrates a reverse offset printing process for use in continuous operation. First, the ink was coated onto a roll blanket to form a thin film. A conventional slot-die coating or spin-coating technique was used in this step because the films must be very thin, normally less than one micrometer, to facilitate patterning. The two coating methods also ensure the maintenance of a good ink surface quality, even in the final patterns. During the off step, the embossed pattern of the cliché takes away unnecessary parts from the ink film on the roll blanket due to the high surface energy (or work of adhesion) of the cliché. Lastly, the pattern left on the roll blanket is transferred to a substrate. During continuous operation, the ink left on the cliché must be removed prior to the subsequent off step. Cliché cleaning involves a wet process with solvents that are compatible with the ink. The wet cleaning process is followed by a drying and re-conditioning process to regain the highly adhesive surface properties.

Conventional clichés are made from glass or silicon wafers using photolithography and etching processes, which provide a high dimensional stability and good edge definition. Fig. 2(a) shows the processes involved in conventional cliché fabrication. The etching process involves both anisotropic etching and isotropic etching to create intaglio patterns on the substrates. Because the blanket deforms into the intaglio patterns under the printing pressure, the etched pattern must have an aspect ratio that exceeds some threshold to avoid conditions in which the blanket touches the bottom of the etched patterns. Disposable clichés were prepared using a UV imprinting method. As shown in Fig. 2(b), an imprinting mold was prepared using photolithography and dry etching. The patterns in the imprinting mold were prepared in a phase opposite that of the cliché. The mold was then imprinted onto a UV resin-coated plastic film. Finally, the imprinted film was released from the mold. This imprinting process may be performed in a continuous manner using a roll mold.

3. Experiments

3.1 Fabrication of the disposable cliché

A master mold was first prepared using photolithography methods and deep reactive ion etching of the Si wafer. The mesh patterns were prepared on this wafer in relief, with an aspect ratio of 1. The master mold formed diamond-shaped mesh patterns with a linewidth and pitch of 3.6 μm and 300 μm, respectively. Release agent (TFOCS, Tridecafluoro-1,1,2,2-tetrahydrooctyl-1-trichlorosilane, United Chemical Technology) was vaporized and deposited on the master mold. The release agent can perform intermediation of the interfacial energy between master molds and replicas for easy and complete demolding. A 150 μm thick PC (polycarbonate) base film for the disposable cliché was prepared and treated with O_2 plasma prior to rinsing thoroughly with deionized water. The film was then dried under a nitrogen gas stream. Three drops of a polyurethane (PU) resin (NI-M101S, Nano-Initiative cop.) were placed at the center of the Si mold, the treated PC film was covered with the Si mold, and the assembly was submitted to rolling pressure using a rubber roller rolled along several random directions. UV curing was carried out over 35 s at a power density of 19.16 mW/cm^2 by applying UV exposure (EVG-R60, EV Group) through the PC film. The disposable cliché was then obtained by gently separating the PC film substrate from the master mold. The depth of the

imprinted pattern was measured by laser confocal microscope (NS-I3000, Nanoscope Systems).

3.2 Reverse offset printing

Transparent conductive electrodes were fabricated using a silver nanoparticle ink (RO ink, Advanced Nano Products Inc.) in a reverse offset printing process. The mean diameter of the silver nanoparticles was around 20 nm. The ink was spin-coated at 4,000 rpm for 10 sec onto a PDMS sheet (silicone blanket, Fujikura). A roll blanket was then rolled over the coated PDMS sheet at a moving speed of 5 mm/s under a printing force of 5 kgf. The roll blanket consists of a metal cylinder and a PDMS sheet (R16, KNW) wrapped around the cylinder. The metal cylinder has 100 mm diameter and 200 mm width. The coated ink film was then transferred onto the roll blanket. The PDMS of the roll blanket was sensitively engineered to provide a surface energy higher than that of the PDMS sheet for coating but lower than that of the cliché. The surface energy can be controlled by adjusting the amount of the curing agent when making PDMS sheet. We found a combination of the two different commercially available PDMS sheets to have a small difference in the surface energy but their surface energies are less than that of the disposable cliché. The roll blanket coated with the ink film was then rolled over the imprinted cliché with a moving speed of 10 mm/s under a printing force of 3 kgf. Finally, the mesh patterns remaining on the roll blanket were transferred to a 50 mm × 50 mm soda lime glass substrate by rolling the roll blanket at a moving speed of 5 mm/s under a printing force of 12 kgf. The electrical conductivity of the printed patterns was measured by first sintering the printed samples in a furnace at 350°C for 30 min. The thermal sintering step evaporated the polymer additives in the ink and promoted interconnection of the Ag nanoparticles.

4. Results and Discussions

Fig. 3(a) shows a photograph of the fabricated disposable cliché. The imprinted cliché maintained its flexibility and could be handled more easily than the silicon wafer. Fig. 3(b) shows the microscopic image of the imprinted patterns measured by optical microscope (Eclipse, Nikon). The imprinted linewidth was about 3.6 μm which is exactly same size of the master mold. But there is some loss in depth which was about 2.3 μm. During UV curing, shrinkage of the resin may reduce the depth of the imprinted patterns. The edge sharpness plays an important role to make clear pattern because the ink film is cut by the shear stress imposed by the edge in the reverse offset printing.[16] If the edge is not sharp, the patterned line may not be same as the master mold. As the ink film does not experience clear fracture, the linewidth can be enlarged by prolonged deformation for releasing the blanket. As shown in Fig. 3(c), the edge was sharp enough to form a clear pattern.

The main function of a cliché used in reverse offset printing processes is to remove residual ink from the non-pattern regions by relying on the high adhesion between the top surface of the cliché and the ink film. Conventional hard clichés may only be substituted by disposable clichés if the disposable cliché surface energy is as large as that of the hard clich. We compared the surface energies of both clichés

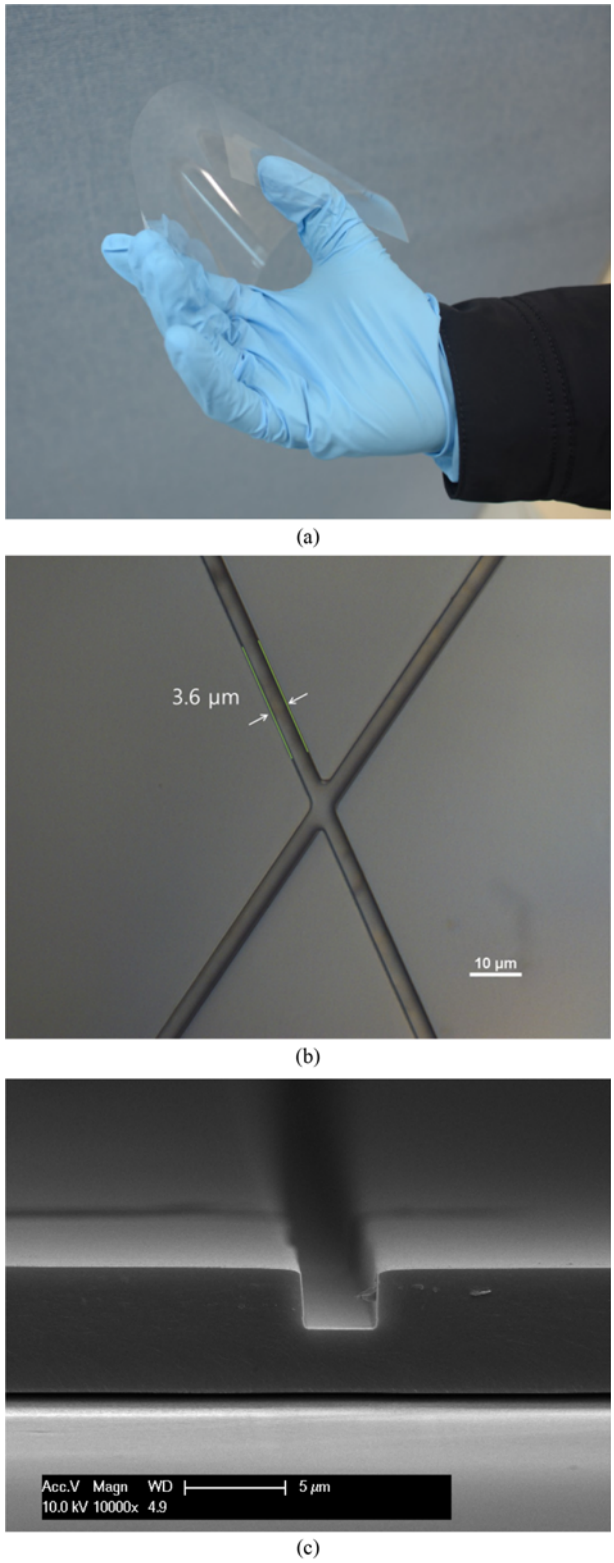


Fig. 3 An imprinted disposable cliché: (a) photograph of a flexible cliché, (b) linewidth of the trench pattern and (c) SEM image of the imprinted mesh pattern

in sessile drop tests that used two types of liquid: water as a polar liquid and diiodomethane as a nonpolar liquid. As shown in Fig. 4, the contact angles on the disposable cliché were smaller than those on the thermally grown SiO_2 layer, which is a typical hard clich's surface

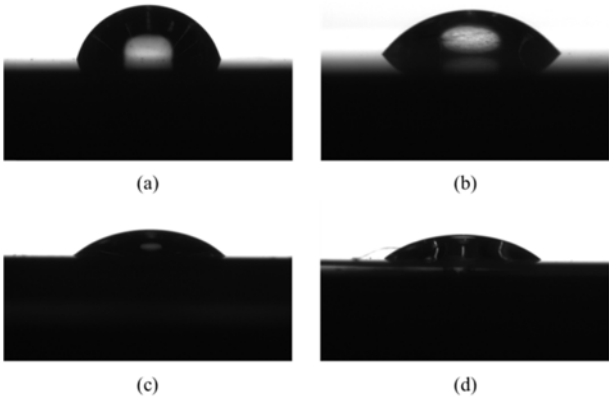


Fig. 4 Contact angles of deionized water: (a) 75° on the SiO_2 cliché, (b) 53° on the disposable cliché; and contact angles of diiodomethane (c) 42° on the SiO2 cliché, and (d) 39° on the disposable cliché

Table 1 Surface energies of the clichés

	Hard clich (SiO_2)	Disposable clich (PU)
Surface energy (mN/m)	43.0	53.6

material. Note that the hard cliché was cleaned using a typical cleaning method of sonication in acetone for 30 min followed by drying with nitrogen gas. Table 1 lists the surface energies of the two materials calculated using the Owens-Wendt geometric mean method.[17] The surface energy of the disposable cliché was even larger than that of the SiO_2 surface. These results suggested that the disposable clich could function as a highly adhesive patterning mask similar to the hard clich.

Fig. 5 demonstrates the off step using the imprinted cliché. Before the off step, the top surface of the imprinted cliché was transparent (the scratches of the specimen holder at the back is seen through) as shown in Fig. 5(a). After off step, it turned opaque except the mesh patterns in Fig. 5(b). The opaque part is the transferred ink film from the roll blanket. The mesh part of the ink film is remained on the roll blanket. Fig. 6 shows a photograph of the metal mesh printed glass substrate. The mesh patterns were invisible to the human eye. The sheet resistance of the metal mesh TCE was about 80 Ω/□. A haze meter (HM-150L2, MCRL) was used to measure the optical properties. Table 2 lists the total transmittance and the haze of the bare glass and the printed TCE. The printed metal mesh TCE yielded a total transmittance of 89.9% and a haze of 1.4%. The electrical and optical properties of the metal mesh TCE were comparable to those of indium-tin oxide (ITO).[18] Fig. 7 shows the transmittance spectra across the UV-VIS range of the bare glass, the metal mesh-printed glass, and the ITO glass, measured using a UV-VIS spectrophotometer (S-3100, Scinco). The metal mesh TCE displayed a flat spectral transmittance across the visible light range whereas ITO displayed some loss in the short wavelength region. These spectral properties were important for obtaining high power efficiency in energy devices or good color reproducibility in display devices. Fig. 8 shows photographic images of the printed patterns. The metal mesh patterns clearly printed without defect. The linewidth was around 3.6 μm and matched the linewidth of the imprinted cliché. This proves that the imprinted cliché gives dimensional stability without any deformation during printing. The surface of the printed metal mesh was very smooth

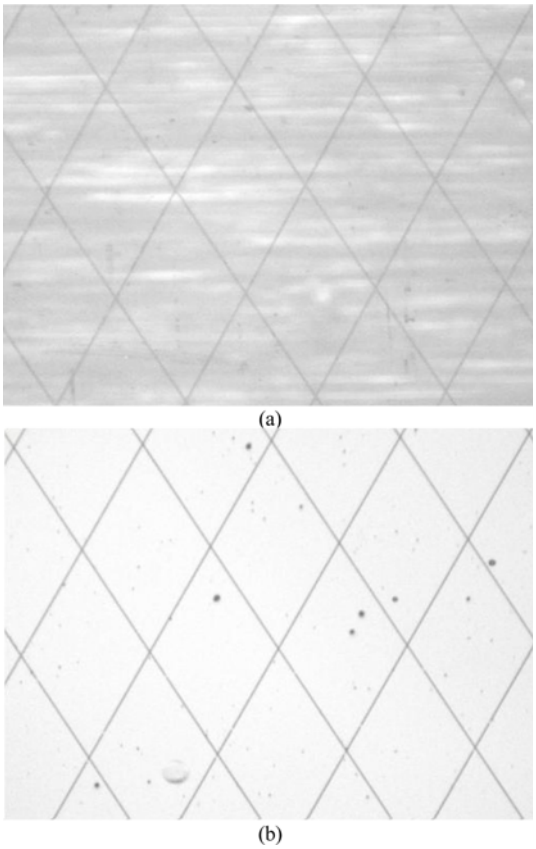


Fig. 5 Surfaces of the imprinted cliché during reverse offset printing: (a) before the off step, (b) after the off step

Fig. 6 Photographic image of a bare glass substrate (left) and a metal mesh-printed glass substrate (right)

Table 2 Optical properties of the bare glass and printed TCE

	Bare glass	Printed metal mesh TCE
Total transmittance (%)	91.6	89.9
Haze (%)	0.2	1.4

because the silver nanoparticles formed a well-organized network after sintering, as shown in Fig. 9. The edges were slightly deformed, most likely because the ink film was cut by the relatively soft edge of the imprinted cliché compared to the hard cliché.

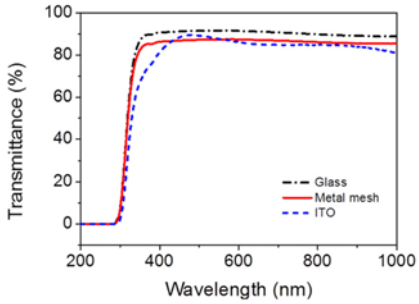
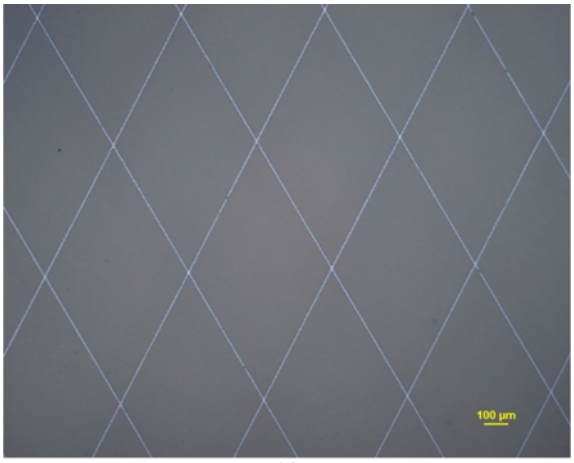
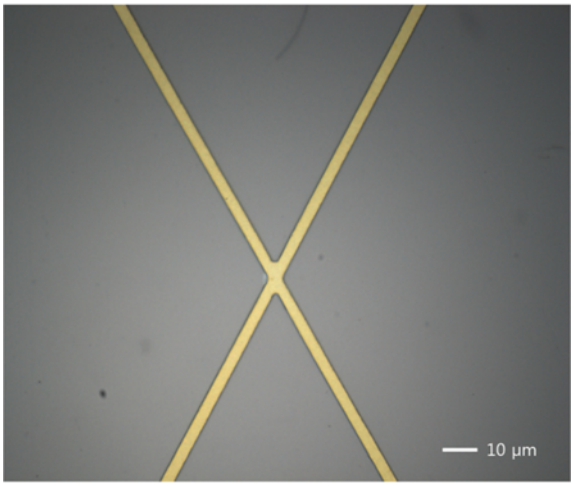


Fig. 7 UV-VIS transmittance spectra of glass, metal mesh, and ITO



(a)



(b)

Fig. 8 Microscopy images of the printed metal mesh (a) 10x magnification (b) 50x magnification

5. Conclusions

Reverse offset printing is a promising technology that may potentially replace photolithography methods. Reverse offset printing techniques have thus far only been implemented in roll-to-plate printing because of the necessity of using hard clichés and the attendant cleaning processes. A continuous supply of flexible disposable clichés would be needed to implement roll-to-roll reverse offset printing. In this paper, we demonstrated that 3.6 μm line patterns could be printed successfully using an imprinted disposable cliché. The ultra-fine lines may be used to prepare highly conductive transparent films, such as touch screen sensors or organic light-emitting diode (OLED) lighting. Although some issues must still be addressed before reverse offset printing may be applied in manufacturing, such as the thermal expansion of the imprinted cliché during use, a disposable cliché technology provides a big step toward the development of a roll-to-roll manufacturing system for preparing electronic devices.

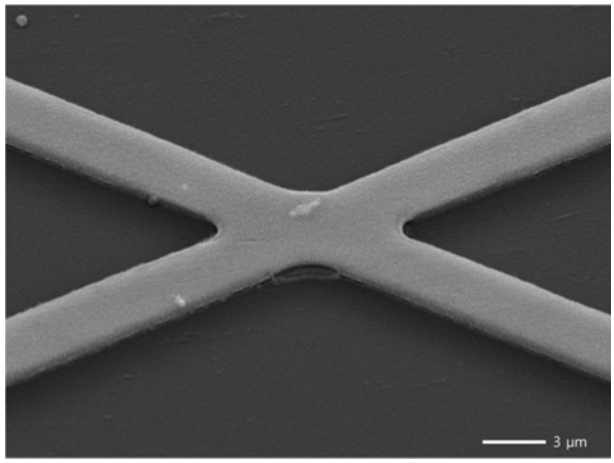


Fig. 9 SEM images of the printed metal mesh

ACKNOWLEDGEMENT

This study was conducted with the generous support of the Ministry of Science, ICT and Future Planning, and Korea Institute of Machinery and Materials. (NK186C, SC1050), and also supported by the Technology Innovation Program (No. 10052802) funded by the Ministry of Trade, Industry & Energy (MI, Korea).

REFERENCES

1. Jeon, S. J., Koo, S. M., and Am Hwang, S., “Optimization of Lead- and Cadmium-Free Front Contact Silver Paste Formulation to Achieve High Fill Factors for Industrial Screen-Printed Si Solar Cells,” Solar Energy Materials and Solar Cells, Vol. 93, No. 6, pp. 1103-1109, 2009.

2. Kim, T. H., Kim, G. L., Jun, Y. H., Lee, G. W., Yeo, K. H., and Yoo, J. M., “Gravure Printing Engraving Roll and Manufacturing Method Therof,” US Patent, No. 20120301605 A1, 2012.

3. Jung, M., Kim, J., Noh, J., Lim, N., Lim, C., et al., “All-Printed and Roll-to-Roll-Printable 13.56-MHz-Operated 1-Bit RF Tag on Plastic Foils,” IEEE Transactions on Electron Devices, Vol. 57, No. 3, pp. 571-580, 2010.

4. Tanaka, M., Mabuchi, Y., Hayashi, T., and Hara, M., “Subtractive Offset Printing for Fabrication of Sub Micrometer Scale Electrodes

with Gold Nanoparticles," Microelectronic Engineering, Vol. 95, pp. 14-20, 2012.

5. Chang, Y. G., Nam, S. H., Kim, N. K., Kook, Y. H., Kim, J., et al., "A Study of RollPrinting Technology for TftLcd Fabrication," Journal of the Society for Information Display, Vol. 17, No. 4, pp. 301-307, 2009.

6. Kim, M., You, I.-K., Han, H., Jung, S.-W., Kim, T.-Y., et al., "Organic Thin-Film Transistors with Short Channel Length Fabricated by Reverse Offset Printing," Electrochemical and Solid-State Letters, Vol. 14, No. 8, pp. H333-H336, 2011.

7. Ryu, G.-S., Lee, M. W., and Song, C. K., "Printed Flexible OTFT Backplane for Electrophoretic Displays," Journal of Information Display, Vol. 12, No. 4, pp. 213-217, 2011.

8. Choi, N., Wee, H., Nam, S., Lavelle, J., and Hatalis, M., "A Modified Offset Roll Printing for Thin Film Transistor Applications," Microelectronic Engineering, Vol. 91, pp. 93-97, 2012.

9. Kusaka, Y., Sugihara, K., Koutake, M., and Ushijima, H., "Overlay of Semi-Dried Functional Layers in Offset Printing for Rapid and High-Precision Fabrication of Flexible Tfts," Journal of Micromechanics and Microengineering, Vol. 24, No. 3, Paper No. 035020, 2014.

10. Choi, Y. M., Kim, K. Y., Lee, E., and Lee, T. M., "16.2: Reverse-Offset Printed Single-Layer Metal-Mesh Touch Screen Panel," SID Symposium Digest of Technical Papers, Vol. 45, No. 1, pp. 197-199, 2014.

11. Lee, A.-R., Kim, I., Kim, K.-Y., Nam, S.-Y., and Choi, Y.-M., "Quantitative Measurement of Ink-Blanket Adhesion for Contact Transfer Printing Inks," Int. J. Precis. Eng. Manuf., Vol. 16, No. 1, pp. 151-156, 2015.

12. Park, J., Park, J. H., Kim, E., Ahn, C. W., Jang, H. I., et al., "Conformable SolidIndex Phase Masks Composed of High-Aspect-Ratio Micropillar Arrays and their Application to 3D Nanopatterning," Advanced Materials, Vol. 23, No. 7, pp. 860-864, 2011.

13. Jang, H.-I., Ko, S., Park, J., Lee, D.-E., Jeon, S., et al., "Reversible Creation of Nanostructures between Identical or Different Species of Materials," Applied Physics A, Vol. 108, No. 1, pp. 41-52, 2012.

14. Park, W. I., Kim, K., Jang, H. I., Jeong, J. W., Kim, J. M., et al., "Directed SelfAssembly with Sub-100 Degrees Celsius Processing Temperature, Sub-10 Nanometer Resolution, and Sub-1 Minute Assembly Time," Small, Vol. 8, No. 24, pp. 3762-3768, 2012.

15. Jeong, J. W., Yang, S. R., Hur, Y. H., Kim, S. W., Baek, K. M., et al., "High-Resolution Nanotransfer Printing Applicable to Diverse Surfaces Via Interface-Targeted Adhesion Switching," Nature Communications, Vol. 5, Article No. 5387, 2014.

16. Choi, Y.-M., Lee, E.-S., Lee, T.-M., and Kim, K.-Y., "Optimization of a Reverse-Offset Printing Process and Its Application to a Metal Mesh Touch Screen Sensor," Microelectronic Engineering, Vol. 134, pp. 1-6, 2015.

17. Owens, D. K. and Wendt, R., "Estimation of the Surface Free Energy of Polymers," Journal of Applied Polymer Science, Vol. 13, No. 8, pp. 1741-1747, 1969.

18. TDK, "TDK ITO Transparent Conductive File FLECLEAR ®," http://product.tdk.com/en/products/film/fleclear/ (Accessed 13 AUG 2015)