Application of Inkjet Technology in Flat Panel Display

Beyong-Hwan Ryu and Youngmin Choi

Advanced Materials Division,
Korea Research Institute of Chemical Technology
P.O.Box 107, Yusung, Taejeon, 305-600, Korea
Phone : +82-42-860-7365 , E-mail : bhryu@krict.re.kr

Abstract

It is expected that the inkjet technology offers prospect for reliable and low cost manufacturing of FPD (Flat Panel Display). This inkjet technology also offers a more simplified manufacturing process for various part of the FPD than conventional process. For example, recently the novel manufacturing processes of color filter (C/F) in LCD, or RGB patterning in OLED by inkjet printing method have been developed. This elaborates will be considered as the precious point of manufacturing process for the mass production of enlarged–display panel with a low price. On this point of view, we would like to review the status of inkjet technology in FPD, with some results on forming micro line by inkjet patterning of suspension type silver nano ink as below.

We have studied the inkjet patterning of synthesized aqueous silver nano-sol on interface-controlled ITO glass substrate. Furthermore, we designed the conductive ink for direct inkjet patterning on bare ITO glass substrate. The first, the highly concentrated polymeric dispersant-assisted silver nano sol was prepared. The high concentration of batch-synthesized silver nano sol was possible to 40 wt%. At the same time the particle size of silver nanoparticles was below 10~20nm. The second, the synthesized silver nano sol was inkjet - patterned on ITO glass substrate. The connectivity and width of fine line depended largely on the wettability of silver nano sol on ITO glass substrate, which was controlled by surfactant. The relationship was understood by wetting angle. The line of silver electrode as fine as 50~100 ㎛ was successfully formed on ITO glass substrate. The last, the direct inkjet-patternable silver nano sol on bare ITO glass substrate was designed also.

1. Introduction

Inkjet printing method is a very useful technology for micro-scale patterning of lines or dots by ejecting tiny droplets of 10~100μm diameter onto a substrate. Recently, a lot of research efforts were devoted to develop inkjet printing method as a patterning tool substituting screen printing and/or photolithography methods for making micron-sized patterns. Inkjet patterning has the following advantages over conventional photolithography methods: [1-4]

(1) It does not require a mask for direct patterning.
(2) It can be easily applied to large-sized substrates.
(3) Materials are used effectively.
(4) Processing time is very short.
(5) The equipment is compact and requires minimal investment.

This inkjet patterning technique would also be useful for forming metal interconnects in flat panel displays, to reduce processing cost especially for PDP and other large size displays [1]. However, in order to obtain enough conductivity for bus and address electrodes of PDP interconnects, it would be necessary to develop a novel conductive ink and/or control its wetting properties on ITO glass substrate. The typical preparation methods of silver nanoparticles for conductive ink are well known, i.e., physical, such as laser ablation, and chemical reaction in solution. Although the conductive ink prepared by physical method has developed already, it needs expensive equipment. Therefore, it would be more favorable to develop direct chemical preparation method for conductive inks.

On this point of view, we would like to review the status of inkjet technology in FPD, i.e. possibility and considered points to be overcome the limitation, with some results on synthesis of silver nano ink and forming micro line by inkjet patterning of suspension type-silver nano ink.

2. Application of inkjet technology

The inkjet technology was applicable to fabrication of dispaly parts classified with ink type as shown in Table 1. In this review, we would like to focus on fabrication of dispaly parts by inkjet printing method with suspension type ink, which was little reported yet.

Table 1. Application of inkjet technology in FPD.

Display/ ink	PDP	LCD	OLED	(FED)
Polymer solution type		-Liquid crystal -Thin film TR circuit	-RGB -Hole/ electron transport	
Suspension type	Elec- trode	-C/F, -Electrode	(C/F)	-Emitter -Electrode

2.1 Electrodes

Silver nano-particle ink was selected as the key material in the inkjet printing process. Nano-silver particles were formed by the gas evaporation method, where metal atoms are evaporated and cooled by collisions with atmospheric gas atoms, which causes them to condense into particles. The silver particles have an average diameter of 3.8 nm and a narrow distribution.

These particles are dispersed into an organic solvent and made to nano-particle ink. An inkjet ink desirably possesses a viscosity of less than 20 mPa▪ s and a surface tension of 20~50mN/m. Especially, a dispersing organic solvent with low vapor pressure that inhibits drying is preferably used for avoiding nozzle clogging. The dispersing organic solvent is tetradecane. Ink contains 60 wt% silver metal and possess a viscosity of less than 20 mPa▪ s. This silver ink exhibits good ejection properties for a Seiko-Epson MACH print head.

The schematic drawing of narrow silver lines formed with the aforesaid conditions was shown in Fig. 1. These 30-μm-wide 0.5-μm-thick silver lines were drawn by placing ink droplets having a diameter of 30 μm on the substrate every 28 μm along the line, i.e. with a 2-μm overlap between adjacent droplets. The resistivity of the silver lines is 2 μΩcm after heating at 300°C for 30 minutes. [4]

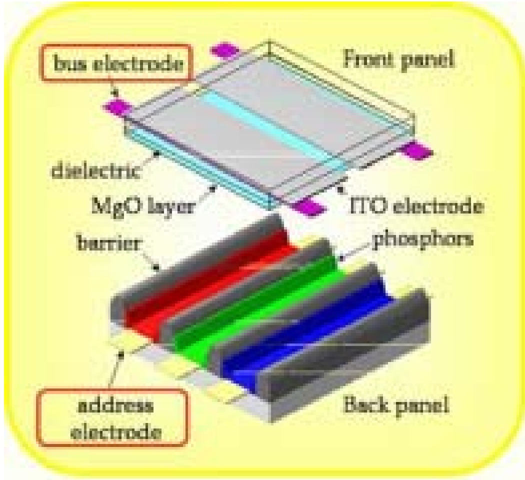

Fig. 1. Illustration of PDP electrodes.

2.2 Color filter

The dramatic growth of liquid crystal display (LCD) has been supported by strong demand for flat color displays in notebook PCs and HDTVs. Portability features such as small outline dimension, thin, light weight, fine resolution and low power consumption has been strongly demanded for notebook PC applications. It is believed that TFT-LCDs will dominate the huge LCD market in multi-media age. Color filter (CF) is an important constituent of liquid crystal display panel. LCD panel has two glass substrates, which are aligned to each other. One is color filter substrate and other is driving substrate. Color filter's pixel has R, G, B color elements and black matrix is located between the colors to avoid leakage of light and photoelectrical conversion in TFT. Liquid crystals are filled between themselves, which are few microns apart. Polarizers are located on the outer sides of the two substrates. The production of the color filter array is a technique-sensitive process. The filter surfaces must be as smooth as possible for maximum color purity and minimum dispersion. They must adhere strongly to the pixel surface.

The C/F is classified by light source as shown Fig. 2. These C/F could be producible by inkjet technology. The RGB light sourced C/F is used generally in OLED. But this system is the brightest, but expensive. The white light sourced C/F is normally used for a generation of RGB color on LCD now. This might be adaptable to OLED to reduce the cost in the future. The blue light sourced C/F could be considerable. But the convertible materials from blue to red or green are still necessary. [5,6]

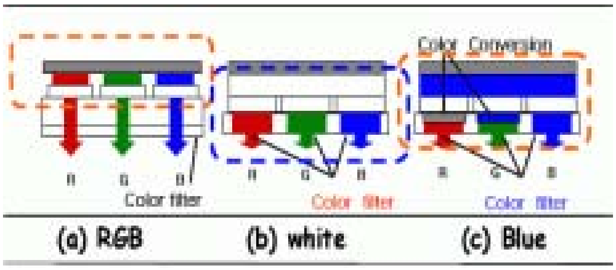

Fig. 2. The color filter system classified by light source on FPD.

3. Status of inkjet technology in FPD

Inkjet technology is generally adaptable to the fabrication of ~50µm width line. To overcome the above limit, i) rheological behavior of ink ejected from nozzle, ii) design of inkjet nozzle including system managing, and iii) wetting property of ink on substrate should be studied systemically.

Therefore, the possibility or limitation of inkjet patterning is depended on the controlling the interfacial properties of materials and substrates, and the accuracy of moving parts of inkjet equipment, which should be closely cooperated together to get synergy effect. [7,8]

4. Synthesis and inkjet patterning of highly concentrated silver nano-sol [9-12]

The objective of this study is to develop novel conductive ink, which enables fabricating several tens of micrometer width ordered lines on ITO glass substrate by inkjet printing, as a key material for flat panel display. For an excellent conductive ink, following two conditions should be satisfied. The first, conductive ink should be consists of particles with narrow size distribution, and their dispersion stability is required for continuous ejecting at inkjet nozzles. The second, highly concentrated silver nano sol is required in order to achieve the fine micro lined-electrode with high conductivity after heat treatment.

In this work, we have carried out the synthesis of highly concentrated silver nano-sol assisted by polymeric dispersant. The complex effect of polyelectrolytes with silver ions on the particle size distribution of silver nano sol was studied. The concentrated silver nano-sol was also prepared with varying of molecular weight of polyelectrolytes and control of initial nucleation and growth of silver nanoparticles, to achieve the dispersion stability and to control the size of silver nanoparticles. Furthermore, the printability of synthesized silver nano-sol on ITO glass substrate was investigated, as well as the relationship between wetting angle and line connectivity of silver nano-sol on ITO glass substrate.

Furthermore, the patterning of synthesized silver nano sol on ITO glass substrate was investigated. We have also tried to find out the relationship between wetting angle and line connectivity of silver nano sol on interface-controlled ITO glass substrate. From these results, we intended to discuss the synthesis condition of nanoparticles as well as the role of polyelectrolytes on the synthesis. The synthesized silver nano sol was patterned on ITO glass substrate by inkjet printing, to explore the possibility of using them as versatile microelectrodes. We also, controlled surface properties of ITO glass substrate by treating them with ionic surfactants. Finally, we studied the relationship between formation of silver nano sol microelectrodes and wetting property of ITO glass substrate.

The last, we were intended to design the silver nano sol which could directly form the fine line on bare ITO glass substrate by the inkjet method.

4.1. Synthesis of highly concentrated silver nano-sol [9-11]

With varying molecular weight (MW), from 1,200 to 30,000, of polyelectrolytes (PE), the role of PE on synthesis of 10wt% silver nano sol was studied. Since reduction potential of noble metals, such as Ag, Pt, and Au is very high, the control of reducing rate of these noble metal ions could be very important to reproduce homogeneous particle size and shape. [13-17]. A polyelectrolytes will play an important role in synthesis of noble metal nanopaticles. The complex effect of COO^- group in polyelectrolytes with Ag^+ ion will help for preparing silver nanoparticles. In case of R=0 (without polyelectrolytes) the particle size is 200~300nm, which is more than 10 times larger than that of silver nanoparticles at R=0.5. To conclude, the ratio of [COO^-] to [Ag^+] is related with the degree of complex formation which affects the particle size and size distribution, Furthermore, the limited migration of Ag^+ ion for reduction results in a control of nanoparticle nucleation and growth. Another important role of polyelectrolyte is contribution to the dispersion of silver nanoparticles after the synthesis. To control the particles size and distribution, the nucleation and crystal growth is very important [8-9], which is controlled by reducing power and reducing speed. The 10~20nm sized Ag nanoparticles can be produced easily by introducing reducing agent slowly.

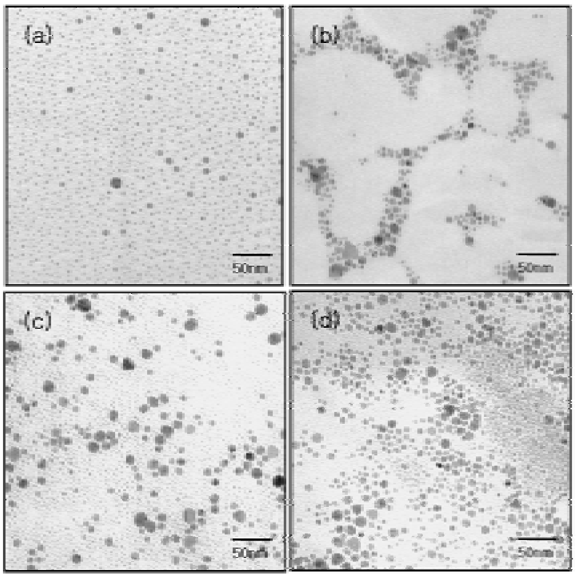

Fig. 3. TEM image of various concentrated silver nano sol synthesized with Mw=15,000; (a) 10 wt% (b) 20 wt% (c) 30 wt%, and (d) 40 wt%.

The highly concentrated silver nano sol from 10 wt% to 40wt% was prepared at R=0.5 as the molar ratio of reducing agent to Ag ion was kept at 2.0. The results showed in Fig. 3. The particle size of all of them was below 10nm, even though the particle size of them increased with increasing concentration. Finally, the highest concentration of batch-synthesized silver nano sol was achieved successfully to 40wt%.

4.2. Inkjet patterning of synthesized silver nano-sol [12]

The 20wt% silver nano sol with smaller than 10nm as shown in Fig. 3(b) was adapted to inkjet patterning of electrode on ITO glass substrate. The rheological behaviors of 10~40wt% Ag nano sol have "thixotropic behavior", which is a relatively high viscosity at low shear rate and a relatively low viscosity at high shear rate. This behavior predicts that the Ag nano sol is easily ejected with low viscosity, and then the fine patterning is easily formed with relatively high viscosity after being ejected through the fine hole in inkjet printer.

A synthesized Ag nano sol was inkjet patterned on interface-controlled ITO glass substrates. We modified the ITO glass substrate with ionic surfactants, such as hexadecanethiol, Diisooctyl sodium sulfosuccinate (AOT) and polyethylnenimine (PEI). The ITO glass substrates were treated in the range of 10~10,000ppm of above surfactants.

In Fig. 4, wetting angle and inkjet pattern of silver nano sol on modified ITO glass substrate with hexadecanthiol were shown. The dot pattern of silver nano sol was formed since the wetting angles increased more than that of origin. In case of Fig. 5, Ag nano sol forms wide line as wide as over a few hundred μm on ITO glass substrates treated with AOT (Diisooctyl sodium sulfosuccinate). It is thought that wide stripe shaped-pattern can be formed due to the low wetting angles of silver nano sol on above substrate.

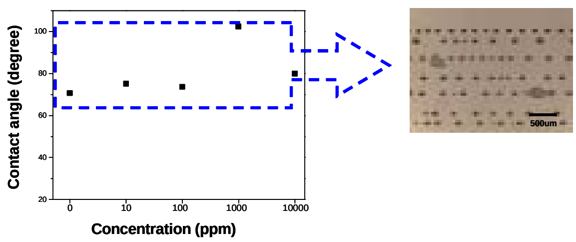

Fig. 4. Wetting angle and inkjet pattern of silver nano sol on modified ITO glass substrate with hexadecanthiol.

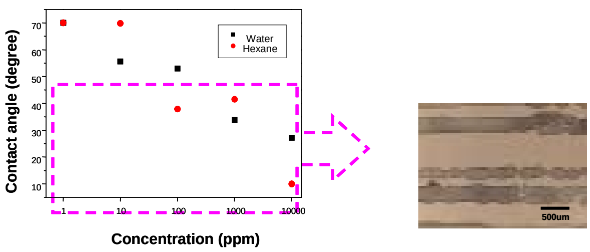

Fig. 5. Wetting angle and inkjet pattern of silver nano sol on modified ITO glass substrate with AOT (Diisooctyl sodium sulfosuccinate).

As a further study, the bare ITO glass substrate was treated with various concentration of PEI in order to improve the wetting property of bare ITO glass substrate. The contact angle was decreased drastically at 10ppm, and saturated slowly after that. Thus, it was found that the proper concentration of PEI on bare ITO glass substrate is about 100ppm as shown in Fig. 6. The contact angles of water and Ag nano sol on 100ppm of PEI treated ITO glass substrate were

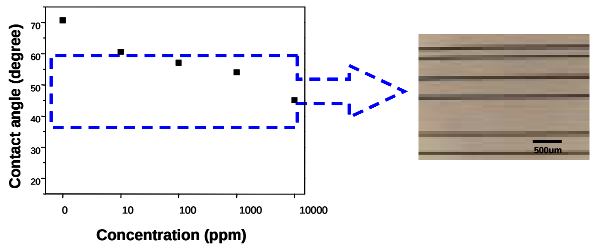

Fig. 6. Wetting angle and inkjet pattern of silver nano sol on modified ITO glass substrate with PEI (polyethynenimine).

dramatically changed from 82.7° and 66.1° to 53.4° and 40.3°, respectively. Also, uniform micro-line with 60~70 µm width was formed on PEI treated ITO glass substrate. This implies that the inkjet patterning of Ag nano sol is improved as the surface property of modified ITO glass substrate has changed to more wettable than that of bare ITO.

4.3. Design of direct inkjet-patternable silver nano-sol

In this part, we designed the direct inkjet-patternable silver nano sol on bare ITO glass substrate by using the polyelectrolyte modified partially hydrophobic, which has wetting angle of 50~60^{o}. The 10wt% synthesized silver nano sol with smaller than 20nm size of nanoparticle as shown typically in Fig.7(a). Also, the direct inkjet-patterning of that silver nano-sol was done on bare ITO glass substrate as shown in Fig. 7(b). As a result, the fine line of 60~70µmwidth was formed directly on bare ITO glass substrate.

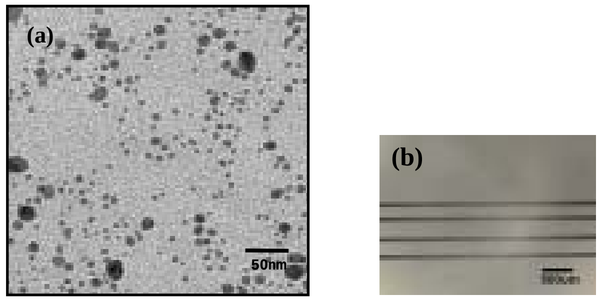

Fig. 7. TEM image of specially designed silver nano sol (a) and optical microscope image of direct inkjet pattern (b) on bare ITO glass substrate by using (a).

5. Conclusion

We have reviewed the status of inkjet technology in FPD. Lots of works still are still remained to be solved. The application of inkjet technology to the delivery of functional materials includes important challenges in terms of ink formulation (or synthesis of ink), print head and print system design, substrate choice and preparation, and control of solvent evaporation. Therefore, the cooperation among them is necessary for creating the synergy effect on solving the problems.

The inks need to be formulated in a narrow viscosity range compatible with the specific print head used. In many cases, the additives that are routinely used in graphic arts printing to modify, for example, ink viscosity, cannot be used for functional materials, as they will adversely affect the performance of materials.

We have studied the synthesis of silver nano sol for inkjet patterning of electrode on ITO glass substrate. We have studied also the inkjet patterning of silver nano sol on ITO glass substrate for making electrodes as follows. The size of silver nanoparticle has been controlled by the Mw and amount of polyelectrolytes as well as adding speed and/or amount of reducing agent. The synthesis of silver nanoparticle assisted with polyelectroyte, which molecular weight is 15,000, was possible in the wide range of R=0.1~1.0. The 10~20nm sized silver nanopaticles were produced in case of the slow adding of reducing agent. The maximum concentration of batch-synthesized Ag nanoparticles was up to 40wt%. The synthesized silver nano sol was adapted to inkjet patterning on ITO glass substrate. The silver micro electrodes with 50~100µm line width were formed on ITO glass substrate treated with 100ppm of PEI. The direct inkjet-patternable silver nano sol on bare ITO glass substrate was designed by using the polyelectrolyte modified partially hydrophobic, which has wetting angle of 50~60^o.

6. Acknowledgements

This work was supported from Information Display R&D Center one of the 21th Century frontier R&D Program funded by the Ministry of Commerce, Industry and Energy of Korea.

The authors deeply appreciate Mr. Han-Sung Park and Mr. Jong-Hoon Byun for their dedicated efforts on this work.

7. References

[1] M. Grove, D. Hayes, R. Cox, D. Wallace, J. Caruso, M. Hampden-Smith, T. Kodas, K. Kunze, A. Ludviksson, S. Pennino and D. Skamser, “Color Flat Panel Manufacturing Using Ink Jet Technology”, Proceedings, Display Works ‘99, (1999)

[2] T. Shimoda, S. Kanbe, H. Kobayashi, S. Seki, H. Kiguti, I. Yudasaka, M,Kimura S. Miyashita, R.H. Friend, J.H. Burroughes and C.R. Towns, “Multicolor pixel patterning of light-emitting polymers by ink-jet printing”, Tech. Digest of SID '99, pp. 376-81 (1999).

[3] S. Miyashita, Y. Imamura, H. Takeshita, M. Atobe, O. Yokoyama, Y. Matsueda, T. Miyazawa and M. Nishimaki, “Invited Full Color Displays Fabricated by Ink-Jet Printing”, Proc. of Asia Display/IDW'01, pp. 1399-1402 (2001).

[4] M. Furusawa, T. Hashimoto, M. Ishida, T. Shimoda, H. Hasei, T. Hirai, H. Kiguchi, H. Aruga, M. Oda, N. Saito, H. Iwashige, N. Abe, S. Fukura, K. Betsui, "Inket-Prtinted Bus and Address Electrodes for Plasma Display", Tech. Digest of SID '02, pp. 753-755 (2002)

[5] Tatsuya Shimoda, Katauyuki Mori, Shunichi Seki, and Hiroshi Kikuchi, “Inkjet Printing of LED polymer Displays”, MRS Bull. Pp. 821-827 (2003)

[6] Kikuchi Hirishi, Miyashita Tarobu, Nakamura Toshio, and Watanabe, “Ink Formulation and preparation of C/F, KR2000-0071813, 2000

[7] Dong-Hoon An, and Hyo-Twak Kwan, “Development and Status of Inkjet Technology”, Korean Information Display Soc., vol. 5. pp. 3-11 (2004)

[8] Rheology Center for Korea Univ., “Application of Rheology in Large FPD”, (2005) pp. 64-70

[9] Beyong-Hwan Ryu, Youngmin Choi, Han-Sung Park, Jong-Hoon Byun, Kijeong Kong, Jeong-O Lee, and Hyunju Chang, " Synthesis of Highly Concentrated Silver Nano Sol and its Application to Ink jet Printing", Colloid and Surfaces A; Engineering Aspects, Accepted (2005)

[10] B.H. Ryu, J.D. Lee, O.S. Lee, Y.C.Kang and H.S. Park, "Synthesis of Highly Concentrated Silver Nanoparticles Assisted Polymeric Dispersant", Key Eng. Materials, vol.264-268, pp.141-142 (2004)

[11] Han-Sung Park, Dong-Soo Seo, Youngmin Choi, Kijeong Kong, Jeong-O Lee, Hyunju Chang, and Beyong-Hwan Ryu, “Synthesis of Concentrated Silver Nano Sol for Inkjet Method”, J.Korean Ceramic Soc.,vol.41, (9) pp. 670~676 (2004)

[12] Jong-Hoon Byun, Dong-Soo Seo, Youngmin Choi, Kijeong Kong, Jeong-O Lee, Hyunju Chang, and Beyong-Hwan Ryu, “Fabrication of Silver Micro Lines by Ink-Jet Method” , J.Korean Ceramic Soc., vol.41, (10) pp. 788~791 (2004)

[13] K. Torigoe, Y. Nakajima and K. Esumi, “Preparation and Characterization of Colloidal Silver-platium Alloys," J. Phys. Chem. 97, pp. 8304-8309 (1993)

[14] Thearith Ung, Michael Giersig, David Dunstan and Mulvaney, "Spectroelectrochemistry of Colloidal Silver," Langmuir, 13[6], pp. 1773-1782 (1997)

[15] Kan-Sen Chou and Chiang-Yun Ren, “Synthesis of Nanosized Silver Particles by Chemical Reduction Method," Materials Chemistry Physis, 64, pp. 241-246 (2000)

[16] L. M. Bronstein, O. A. Platonova, A. N. Yakunin, I. M. Yanovskaya and P. M. Valetsky, "Complexes of Polyelectrolyte Gels with Oppositely Charged Surfactants: Interaction with Metal Ions and Metal Nanoparticle Formation," Langmuir, 14[2], pp. 252-259 (1998)

[17] Mathias Brust, Christopher J. Kiely, "Some recent advances in nanostructure preparation form gold and silver particles: a short topical review", Colloids and Surfaces A: Physicochem. Eng. Aspects, pp. 202, pp. 175-186 (2002)