Printability of synthesized Silver Nano sol in Micro-patterning of Electrode on ITO Glass

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Abstract

We have studied a printability of synthesized silver nano sol on ITO glass substrate. The highly concentrated polymeric dispersant-assisted silver nano sol was prepared by variation of molecular weight and control of initial nucleation and growth of silver nanoparticles, to achive dispersion stability and controlling the size of silver nanoparticles. The synthesized silver nano-sol was tested for printability to explore the possibility of micro-electrodes patterning on ITO glass substrate. The silver micro-electrode with 50~100㎛ line width was formed on ITO glass substrate.

1. Introduction

Inkjet printing method is a very useful technology for micro-scale patterning of line or dot by ejecting tiny droplets 10~100μm in diameter onto a substrate. Recently, much research efforts were devoted to develop inkjet printing method as a patterning tool substituting screen printing and/or photolithography methods for making micron-size ordered patterns. Inkjet patterning has the following advantages over conventional photolithography methods:
(1) It does not require a mask for direct patterning.
(2) It is easily applied to large-size substrates.
(3) Materials are used extremely effectively.
(4) Processing time is 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 PDP bus and address electrode interconnects, it would be necessary to develop a novel inkjettable 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. The conductive ink has been prepared by physical method already [1]. But, preparation by physical method needs expensive equipment, thus it would be more favorable to develop direct preparation of conductive ink by chemical method [2].

The objective of this study is developing a novel conductive ink for inkjet printer making several tens of micrometer width ordered line on ITO glass substrate, as a key material for flat panel display. For the excellent conductive ink, following two conditions must be satisfied. The first, mono-dispersed size and its 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 Ag nanoparticles 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 get dispersion stability and to control the size of silver nanoparticles.

From these results, we intended to discuss the synthesis condition of nanoparticles and the role of polymeric dispersant 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 various surfactants, such as ionic, and non-ionic surfactants. Finally, we studied the relationship between formation of silver nano sol microelectrodes and wetting property of ITO glass substrate.

2. Experiment

Highly concentrated silver nano sol was prepared from $AgNO_3$ (reagent; 99+%, Aldrich) as Ag source materials with $NaBH_4$ and Hydrazine monohydrate (reagent; 97%, $H_2NNH_2 \cdot H_2O$, hydrazine, Aldrich) as reducing agent. The polymeric dispersant (Polyacrylic Ammonium salt; Mw = 1,500~30,000, Aldrich) was used as the best assisting material to prepare silver nanoparticles in preliminary experiment.

The colloidal silver sol was perepared as followed. Ice cold solution of $AgNO_3$ (10~30wt% calculated as Ag) containing various molecular weight (Mw) of polymeric dispersant (polyelectrolytes) was reduced by slow adding of hydrazine monohydrate and/or $NaBH_4$. The formation of Ag (0) nanoparticles was confirmed by UV spectrometer, XRD (X-ray radiation equipped with monochrometer, model: D8 Discover, Cu Kα, Bruker Co,) and FE-TEM (EM912, Carl Zeiss, Germany, installed at Korea Basic Science Institute). The particle size and zeta potential of silver nano sol were measured by the Zetasizer (ELS-800, Otsuka, Japan) after diluting them by 10,000 times. The printability of silver nano sol was explored by using custom- made inkjet printer. Bare ITO glass substrates, surfactant-modified ITO glass, and slide glass were used as substrate for inkjet printing, to compare the printability.

The contact angle of water and synthesized silver nano sol, contained with an anionic poyelectrolytes, measured by contact angle analyzer (Phoenix-300, SEO, Korea). In case of modified ITO glass substrate, Polyethylenimine (PEI; $H(-NHCH_2CH_2-)_nNH_2$, Aldrich) and other non-ionic surfactants were used after diluting them to 10~10,000ppm with distilled water. To prepare the printing substrates, the ITO glass substrates were modified by dipping them in each diluted surfactant solution for 2h, and then followed by drying at 80℃ for 12 h. The micro line of silver nano sol on the proper substrate was fabricated by on-demanded type inkjet printer, and then observed by optical microscope (ICS-305A, Sometech, Korea) with 300 magnifications.

3. Results and discussions

3.1. Synthesis of highly concentrated Silver Nano-sol

With varying molecule weight of polyelectrolytes (PE), the role of PE on synthesis of 10wt% silver nano sol was studied. The Ag nanoparticles were characterized by FE-TEM and particle size analyzer as the Mw of PE varied from 1,200 to 30,000. As the results, the particle size of Ag nano sol synthesized using the PE (Mw=15,000, R=1) was typically kept under 20 ~ 100nm as shown in Fig.1.

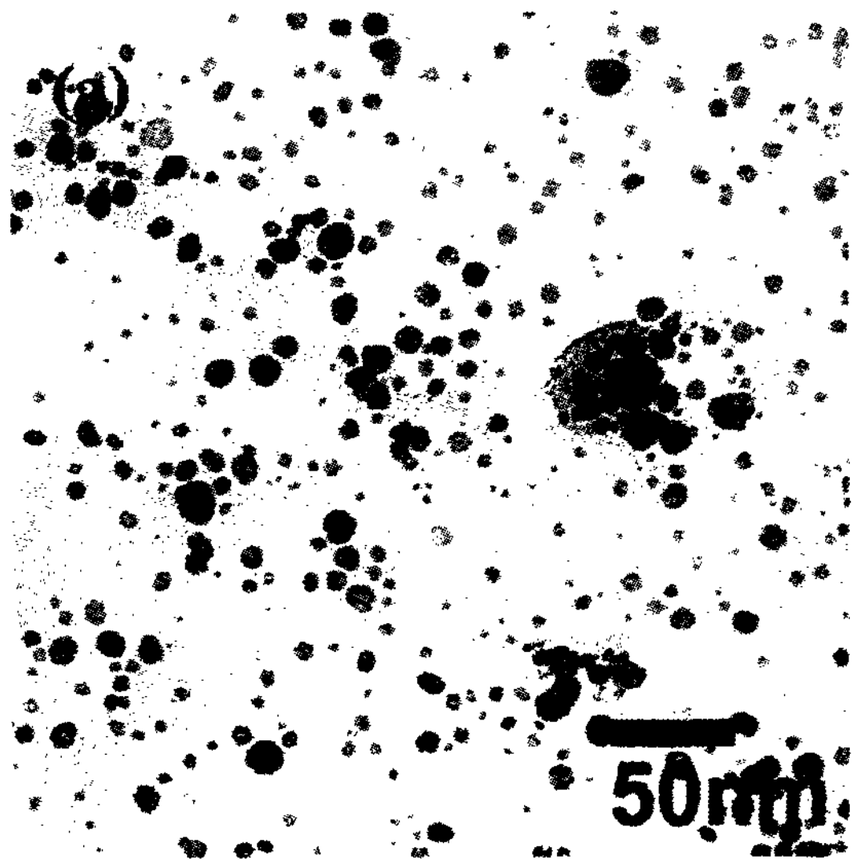

Fig. 1. TEM image of sliver nano sol prepared with the equivalent ratio of polyelectrolyte to silver ion. (R=1).

From the XRD pattern analysis, only Ag (0) was prominent in synthesized products. The highly concentrated Ag nano-sol was successfully synthesized by assisting polymeric dispersant as follows: The complex effect of COO^- group in polyelectrolytes with Ag^+ ion will help for preparing silver nanoparticle, since the limited migration of Ag^+ ion for reduction results in control of nucleation and growth. Furthermore, the polyelectrolytes, in which every segment have anionic functional groups, have relatively more anionic group compared with simple surfactant. Thus, the 10~20nm sized Ag (0) nanoparticles can be produced easily by adding reducing agent slowly, since the agglomeration and crystal growth can be controlled by less amount of polyelectrolytes, though. It was considered that the polymeric dispersant provided the proper nucleation at initial stage and affected sufficient charge density on

Ag nanoparticles resulted in stabilizing of Ag colloids. The molecular weight of 15,000 was the best at R=0.1~1.0 as shown in Fig. 2. It is found out that the size and dispersion stability of Ag nano sol have depended largely on molecular weight and control of initial nucleation and growth of silver nanoparticles. The possible concentration of batch-synthesized silver nanoparticles was up to 30wt%.

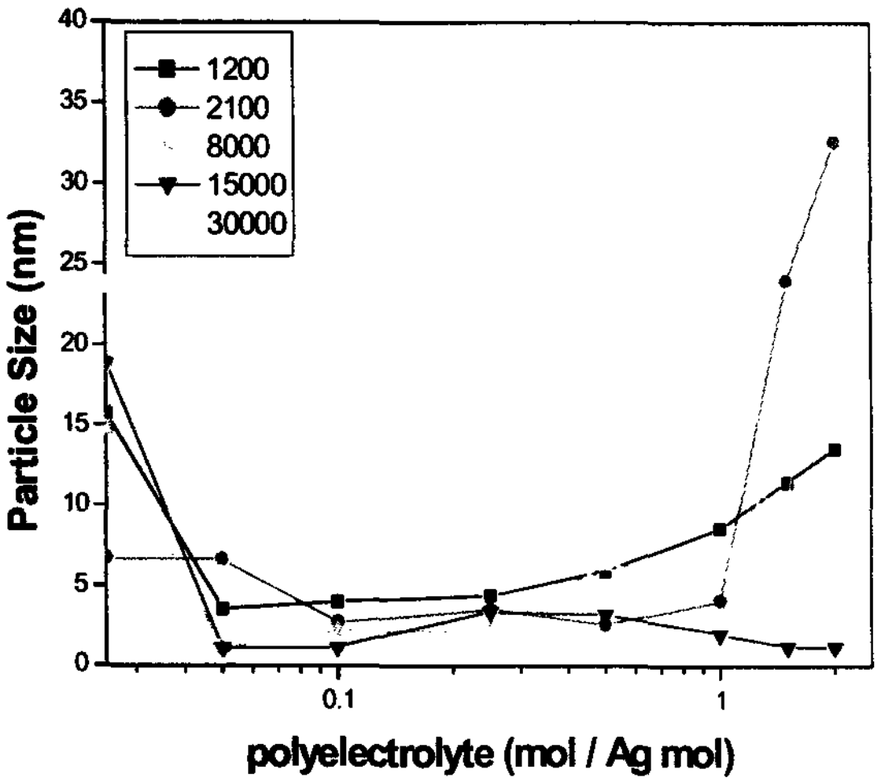

Fig. 2. Particle size of sliver nano sol prepared with variation of adding amount and Mw of polyelectrolytes.

3.2. Printability of Synthesized Silver Nano-sol

The 10wt% synthesized silver nano sol with smaller than 10nm as shown in Fig.1 was tested to explore the possibility of micro-patterning of electrode on ITO glass substrate. The fine line of silver electrode as fine as 50~100㎛ was formed on ITO glass substrate. It is found that the synthesized silver nanoparticles have good dispersion stability, due to the surface charge of –45mV acquired from added polyelectrolytes. The rheological behavior of 10wt% Ag nano sol has a "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 micro line is easily formed with relatively high viscosity after being ejected through the fine hole in inkjet printer.

A synthesized Ag nano sol was patterned on ITO glass substrates by inkjet printing. The contact angles of water and Ag nano sol on three kinds of substrates were investigated as shown in Fig. 3. The contact angle shows the wettability of liquid on solid. For example, the low contact angle means high wettability. The contact angle of water and Ag nano sol were as low as 27.1°and 21.6° for glass substrate, while as high as 82.7°and 66.1° for bare ITO glass substrate, respectively.

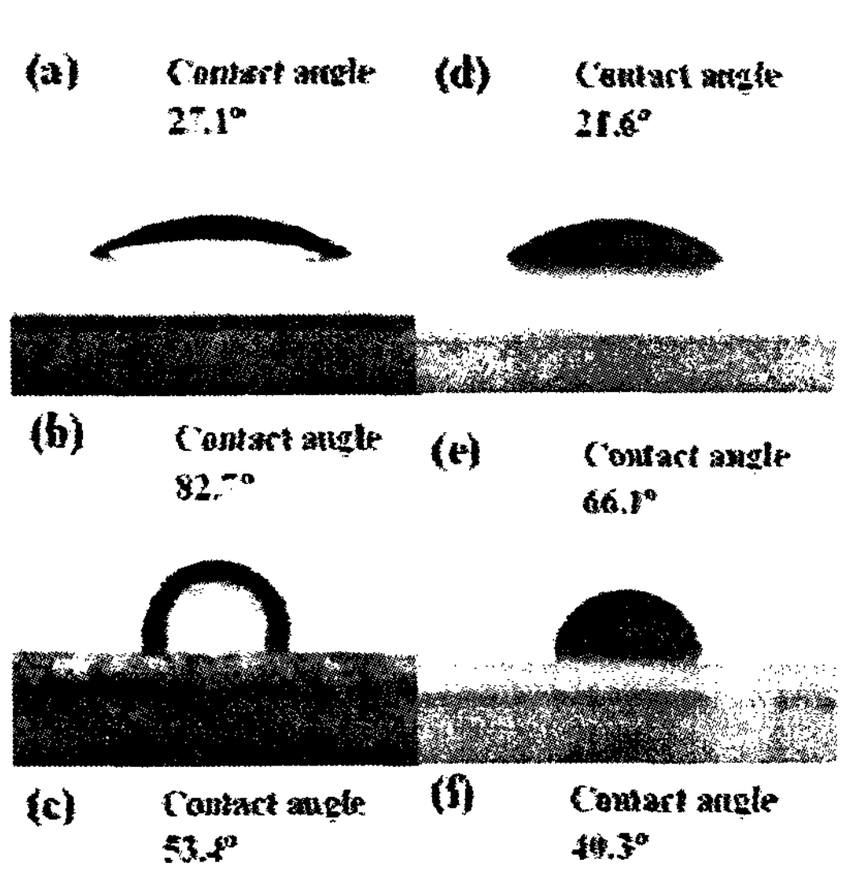

Fig. 3. Contact angle of water drop (a, b, c) and silver nano sol drop (d, e, f) on different substrate;
(a), (d) slide glass, (b), (e) bare ITO substrate and
(c), (f) ITO substrate treated with 100ppm PEI.

The wettablity of aqueous Ag nano sol has almost the same as that of water, but the wetting behavior of bare ITO glass substrate is quite different from that of slide glass substrate. The Ag nano sol was printed on glass substrate by a inkjet printer, then relatively thick line as thick as 100 ㎛ line was formed because the wettability of Ag nano sol was good.
As shown in Fig.4(a), Ag nano sol forms dots as large as over 100 ㎛ on bare ITO glass substrates. Due to the high wetting angles of water and Ag nano sol, only dot- shaped patterns can be formed on bare ITO glass substrate. To improve wettability of bare ITO glass substrate, we have treated bare ITO glass substrate

with 100ppm of PEI. The contact angles of water and Ag nano sol on 100ppm of PEI treated ITO glass substrate were dramatically changed from 82.7° and 66.1° to 53.4° and 40.3°, respectively. Also, uniform micro-line with 60 ㎛ width was formed on PEI treated ITO glass substrate as shown in Fig. 4 (b). This implies that the printability of Ag nano sol was improved as the surface property of modified ITO glass substrate has changed to more wettable than that of bare ITO.

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.

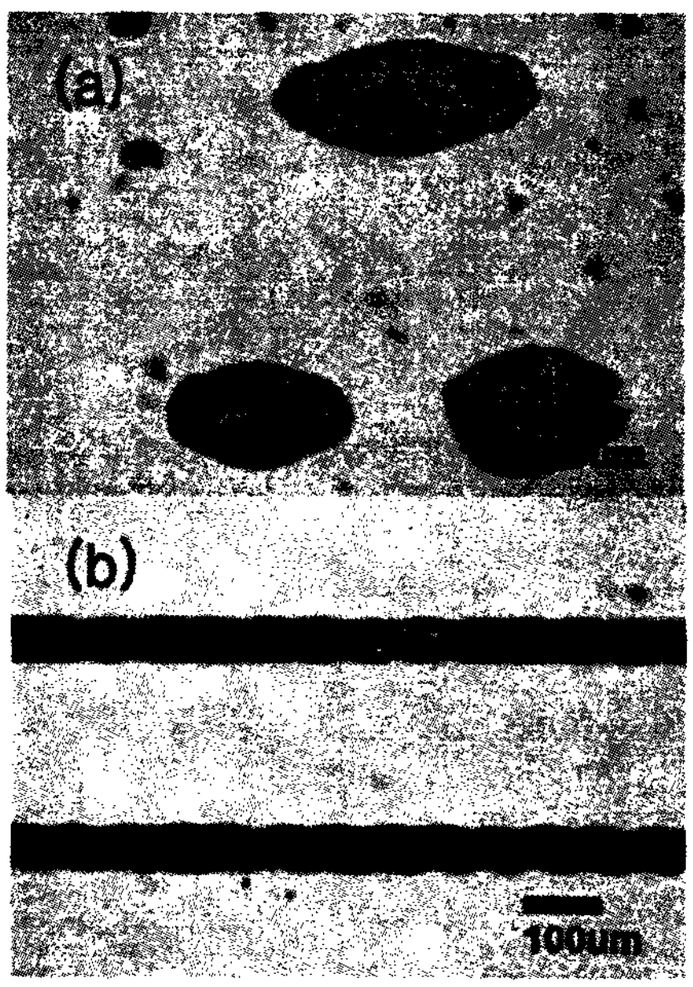

Fig. 4. Optical microscope images of silver nano sol microlines on different substrates (×300).

(a) bare ITO glass substrate

(b) ITO glass substrate coated with 100ppm PEI

4. Conclusion

We have studied a printability of synthesized silver nano sol on ITO glass substrate for micro patterning of electrodes. The size of Ag nanoparticle has depended largely on the Mw and amount of polyelectrolytes as well as adding speed and/or amount of reducing agent. The molecular weight of 15,000 was the best at R=0.1~1.0. The 10 ~ 20nm sized Ag (0) nanopaticle was produced in case of the slow adding of reducing agent. The possible concentration of batch-synthesized silver nanoparticles was up to 30wt%.

The synthesized silver nano sol was tested for printability to explore the possibility of micro electrode patterning on ITO glass substrate. The silver micro electrodes with 50~100㎛ line width were formed on ITO glass substrate treated with 100ppm of PEI.

5. Acknowledgements

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6. References

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