Inkjet patterning of Aqueous Silver Nano Sol on Interface-controlled ITO Glass

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Abstract

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 by variation of molecular weight and control of initial nucleation and growth of silver nanoparticles. 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 fine 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

Recently, lots 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. This inkjet patterning technique would also be useful for forming metal interconnects in flat panel displays, to reduce processing cost especially for plasma display (PDP) and other large size displays. 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. [1-4].

In this work, we have carried out the synthesis of highly concentrated silver nanoparticles assisted by polyelectrolytes. The complex effect of silver ions with them on the particle size distribution of silver nano sol was studied. The highly concentrated silver nano sol was also prepared with varying of molecular weight of polyelectrolytes. We can achieve the stable silver nano sol and control the size of silver nanoparticles.

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.

2. Experiment

Highly concentrated silver nano sol was prepared from $AgNO_3$ (reagent; 99+%, Aldrich) as silver source materials with $NaBH_4$ and/or hydrazine monohydrate (reagent; 97%, $H_2NNH_2 \cdot H_2O$, hydrazine, Aldrich) as reducing agent. The polyelectrolytes (polyacrylic ammonium salt, Aldrich) was used as the best assisting material to prepare silver nanoparticles. The colloidal silver sol was prepared as followed. Ice cold solution of $AgNO_3$ (10~40wt% Ag) that contains various molecular weights (Mw) of polyelectrolytes was reduced by adding hydrazine monohydrate and/or

$NaBH_4$ slowly. The formation of Ag (0) nanoparticles was confirmed by FE-TEM (EM912, Carl Zeiss, Germany). 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 inkjet patterning of silver nano sol was proceeded by using custom-made inkjet printer. Bare and surfactant-modified ITO glass substrates, and slide glass were used as substrate for inkjet patterning. The contact angle of water and synthesized silver nano sol, which containing anionic poyelectrolytes, on substrates was measured by contact angle analyzer (Phoenix-300, SEO, Korea). In case of modified ITO glass substrate, i.e., hexadecanthiol, AOT (Diisooctyl sodium sulfosuccinate) and polyethylenimine (PEI; $H(-NHCH_2CH_2-)_nNH_2$, Aldrich) were used after diluting them to 10~10,000ppm with distilled water. To prepare the modified substrates, the ITO glass substrates were dipped in each diluted surfactant solution for 2h, and then followed by drying at 80℃ for 12h. The micro lines of silver nano sol on the proper substrate were fabricated by on-demanded type inkjet printer, and then observed by optical microscope (ICS-305A, Sometech, Korea) with 40 times magnifications.

3. Results and discussions

3.1. Synthesis of highly concentrated Silver Nano-sol

With varying molecule weight, 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. [5-7]. The 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.

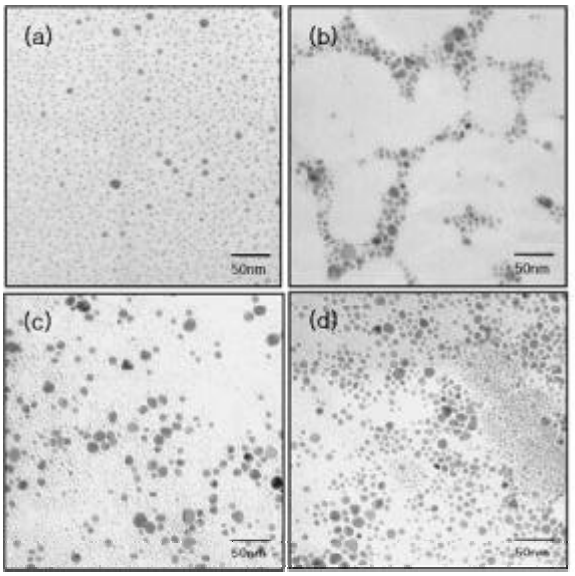

Fig. 1. TEM image of various concentrated silver nano sol synthesized with Mw=15,000; (a) 10 wt% (b) 20 wt% (c) 30 wt%, and (d) 40 wt%.

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. 1. 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%.

3.2. Inkjet Patterning of Synthesized Silver Nano-sol

The 20wt% silver nano sol with smaller than 10nm as shown in Fig. 1(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. 2, 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. 3, 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.

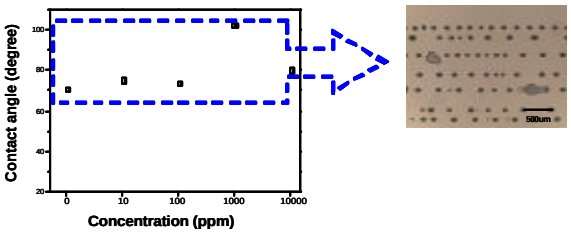

Fig. 2. Wetting angle and inkjet pattern of silver nano sol on modified ITO glass substrate with hexadecanthiol.

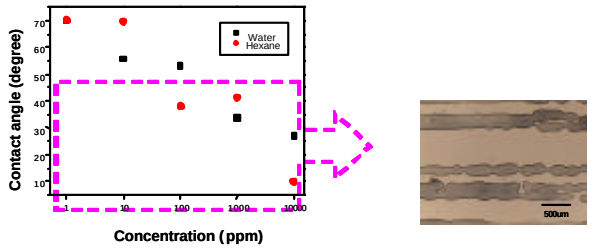

Fig. 3. Wetting angle and inkjet pattern of silver nano sol on modified ITO glass substrate with AOT (Diisooctyl sodium sulfosuccinate).

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. 4. The contact angles of water and Ag nano sol on 100ppm of PEI treated ITO glass substrate were

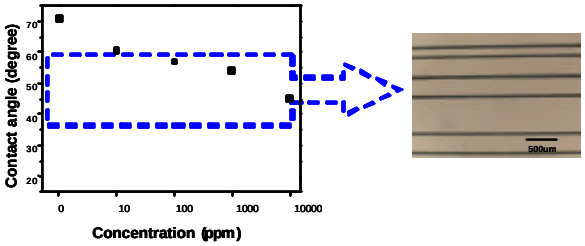

Fig. 4. Wetting angle and inkjet pattern of silver nano sol on modified ITO glass substrate with PEI (polyethynenimine).

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.

3.3. 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°. 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 60~70μm width was formed directly on bare ITO glass substrate.

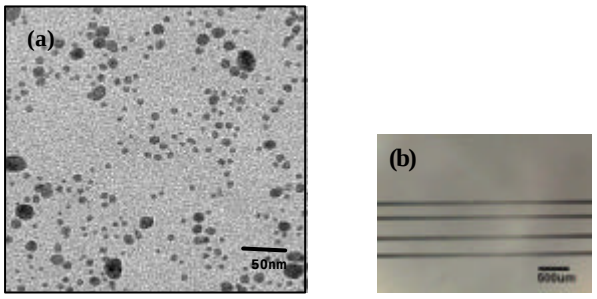

Fig. 5. TEM image of specially designed silver nano sol (a) and optical microscope image of direct inkjet pattern (b) on bare ITO glass substrate by using (a).

4. Conclusion

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.

The size of silver nanoparticle has been depended largely on 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 (0) 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 50~100㎛ 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°.

5. Acknowledgements

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6. References

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