Korean J. Chem. Eng., **25**(6), 1358-1361 (2008)

Screen printing of silver nanoparticle suspension for metal interconnects

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(*Received 2 October 2007 • accepted 2 April 2008*)

Abstract−Silver nanoparticle suspensions were synthesized by chemical reduction method using a formaldehyde reductant. Polyvinyl pyrrolidone (PVP) of two different molecular weights (M.W.=8,000 and 29,000) was used as a stabilizer for the suspensions. PVP of a smaller molecular weight could produce silver suspensions of nanoparticle size around 20 nm. Water-based conductive silver inks with different silver concentrations were prepared and tested for suitability for screen printing. We have successfully printed silver metal lines on glass substrates using a 400 mesh screen-mask with 60wt.% silver ink prepared in this study. Curing at a low temperature of 200 °C for an hour was found sufficient to reach the lowest resistivity value with the synthesized ink. For a line with a width and thickness of 0.5 mm and 2.12 μm, respectively, it exhibited a resistivity of 3.3×10^{-5} Ω·cm, which could serve as conducting lines for various electronic applications.

Key words: Silver Nanoparticle, Screen Printing, PVP, Conductive Ink

INTRODUCTION

Conductive metal lines have been conventionally fabricated by electroplating and etching processes accompanied by lithography technology in the printed circuit board (PCB) industry. Since the process is time consuming and requires many complicated steps, direct printing of conductive metal lines has attracted much attention in recent years. Among the direct printing processes, inkjet printing is studied the most intensively for the fabrication of conductive lines [1-3]. Even though inkjet printing is generally recognized as one of the most promising alternatives for the process, traditional screen printing is also adopted as an alternative since it is a cost-effective and more versatile fabrication technique. Similar to inkjet printing, screen printing allows a great reduction in materials usage and the conductive lines to be printed onto various substrates in one step. Unlike inkjet printing, however, screen printing could bring simplicity, affordability, speed, and adaptability to the fabrication process for conductive lines. For screen printing, the characteristics and quality of printed conductive lines are greatly affected by many printing variables, such as printing speed, angle and geometry of the squeegee, distance between the screen mask and substrate, mesh and squeegee material, *etc.* [4].

For printing processes using conductive inks, several materials have been studied including molten metal, conducting polymers and metallic nanoparticle suspensions [5]. Among them, metallic nanoparticle suspensions have gained significant interest in recent years not only because they can be processed at room temperature [6], but also they show better performance in terms of the electrical conductivity compared with other conducting ink materials. Viscosity and surface tension are the two most important properties of conductive inks [7]. In addition, the physical properties of metallic nanoparticles undoubtedly affect the performance of the product to a great extent. Due to their high conductivity and thermal stability, gold and silver nanoparticle suspensions were widely used in the studies of conductive ink. In this paper, silver nanoparticle suspensions dispersed into water and diethylene glycol were used as the conductive ink for screen printing. Proper mesh count and concentration of silver ink were tested for the screen printing process.

Silver nanoparticles synthesized by the chemical reduction method have been reported in the literature [5,6]. The screen printing of the silver ink has been utilized for bus lines in order to reduce the electrical resistance of the transparent conducting oxide electrode such as ITO in the display industry. The utilization of the silver nanoparticles can effectively reduce the temperature for the post-heat treatment. Here, in this study, we have synthesized the silver nanoparticles and studied the optimum process conditions for the screen printing of the silver nanoparticle ink, such as the silver content of ink, screen mesh count, and the temperature for the post-heat treatment. The screen printing of silver nanoparticle ink studied in this study can be utilized for preparing the auxiliary bus lines of the ITO electrode in the flat panel displays.

EXPERIMENTAL

Silver nanoparticle suspensions were prepared by using 0.05 M silver nitrate ($AgNO_3$) solution as the precursor in this study. Formaldehyde (HCHO, 37% in water) was used as the reducing agent and poly(N-vinyl-2-pyrrolidone) (PVP) as the stabilizer for the silver nanoparticle suspensions. The stabilization of silver suspension is known to be done by its steric effect. Molar ratio of formaldehyde to silver was fixed at 8 in this experiment. After sufficient stirring of the mixed solution, sodium carbonate (Na_2CO_3) solution was then added to promote the reduction reaction at a temperature of 70 °C. The weight ratio of added Na_2CO_3 to silver was fixed at 0.0625. The stabilizer, PVP, with molecular weights of 8,000 and 29,000 was used and compared for the size of synthesized silver nanoparticles and the stabilizing capability of silver suspensions. The weight

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ratio of PVP to silver was fixed at 2 throughout this experiment.

After completion of reaction, the PVP-protected silver colloids were separated from solution by adding acetone and removing after phase separation. The black gel-like material obtained was then washed twice by acetone/water (3/1 volume ratio) solution to remove PVP as much as possible. After the product was dried, it could be re-dispersed in diethylene glycol (DEG) solution with water (50 : 50 wt%) to prepare silver printing inks. Inks with different silver concentration (20, 30, 40, and 60 wt%) were checked for their capability for screen printing.

Glass slides were used as substrates. Screen printing was carried out with different mesh counts' screen (200, 325, 400) to form conductive silver lines with different widths (0.5, 1.5, 2.5, 3.5, 4.5, 5.5 mm). After screen printing, the substrates were first dried in an oven at 70 °C for 5 min to remove solvents and then heated further at two different temperatures of 200 °C and 260 °C for different times (5, 10, 15, 20, 40, and 60 min). The samples were then subjected to be analyzed by both scanning electron microscopy (SEM) and energy dispersion spectrometer (EDS) techniques to examine their microstructures, chemical elements as well as precise thickness measurement.

RESULTS AND DISCUSSION

It has been known that both Na_2CO_3 and NaOH can promote the reduction reaction of silver ion by formaldehyde, but the reaction paths are apparently different [8]. While Na_2CO_3 produces a reaction intermediate of Ag_2CO_3, an intermediate of Ag_2O is formed when NaOH is used to promote the reduction reaction. Comparing the two reduction paths, the rate of reduction reaction is known to be slower when a reaction promoter NaOH is used. Chou et al. [8] have speculated that a smaller size of PVP could probably arrange to provide better coverage on the surface of silver nanoparticles than the larger size of PVP does. In this study, we have used Na_2CO_3 as the reaction promoter to reduce the rate of reaction in order for lower molecular weight PVP to have sufficient time to cover the synthesized silver nanoparticle surfaces. In this way, we have presumed that we could use the lower molecular weight PVP as the stabilizer of silver suspensions, and in turn we could achieve lower resistivity of silver metal lines formed after the screen printing of the suspensions. As we expected, the experimental results revealed that a smaller particle size of silver was synthesized when lower molecular weight of PVP was used. As shown in Fig. 1, the majority of silver nanoparticles were around 30 nm when PVP with molecular weight of 8,000 was used as the stabilizer. When the higher molecular weight PVP (M.W.=29,000) was used, the average particle was found to be about 80 nm. We have also identified that the nanoparticles are pure silver by EDX analysis.

The viscosity of silver nanoparticle suspensions increases with silver content. At low concentrations of suspensions, the viscosity increases linearly with silver content. However, as the silver concentration of the suspensions continues to increase, the interaction between silver nanoparticles is no longer negligible and the viscosity increases rapidly [9]. Therefore, it is almost impossible to achieve screen printing by using a silver nanoparticle suspension with low silver content, in that screen printing requires an appropriate viscosity of the ink. On the other hand, it is also difficult to carry out

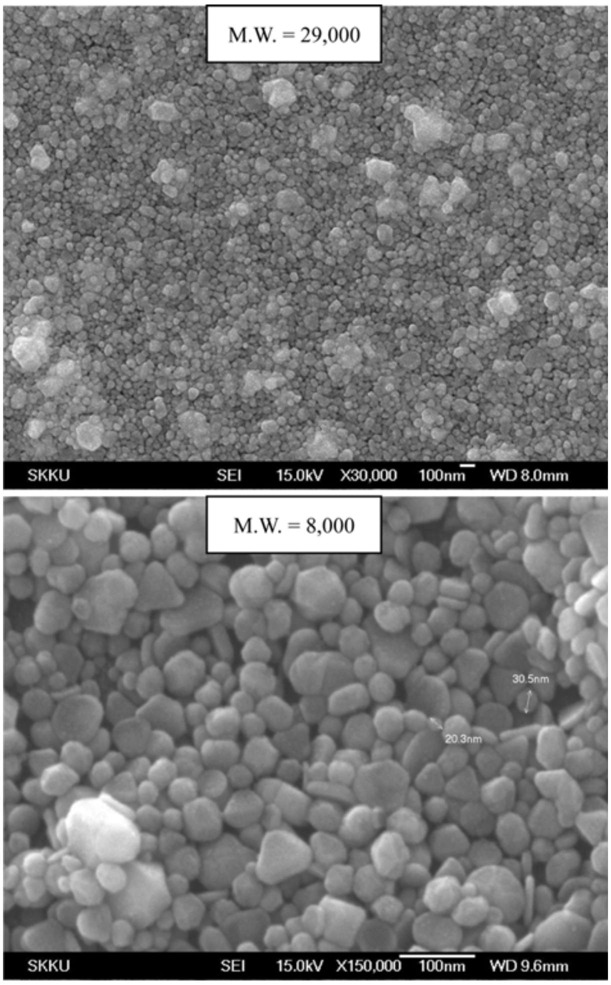

Fig. 1. SEM images of silver nanoparticles synthesized by two different molecular weights of PVP.

screen printing using silver ink with water solvent only, since the silver ink with water solvent only cannot provide adequate viscosity for printing. An organic solvent like DEG helps to reduce the evaporation rate of the ink and also provides the ink with proper viscosity and surface tension for screen printing. For silver screen-printing ink, the silver content was varied from 20 to 60 wt% before an optimal value was determined for screen printing. We showed several silver metal lines with six different widths (0.5, 1.5, 2,5, 3.5, 4.5, and 5.5 mm) formed by the screen printing in Fig. 2. As shown in the figure, the printed lines become continuous regardless of the width as the silver content increases from 30 wt% to 60 wt%. At lower silver content less than 60%, the amount of silver seems to be insufficient to form continuous silver lines. One thing to note here is that at lower silver content the edges of the printed lines look spread out with the ink due to its lower viscosity.

For screen printing of the nanosized silver inks, a hard and square-edge polyurethane squeegee was used. For this study, three different mesh-counts' screens (200, 325 and 400 mesh size) were used for the screen printing. Here the mesh count means the number of holes per square inch. The 400 mesh-counts' screen means that it has 400 holes per square inch, so that the size of openings should be about 63 μm if the thread diameter is 20 μm. Screen-printed silver

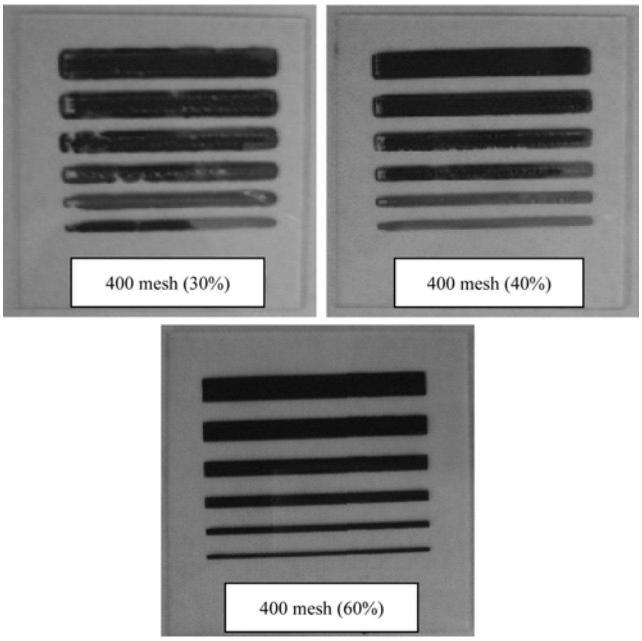

Fig. 2. Photographs of screen-printed silver metal lines printed by using inks with three different silver contents.

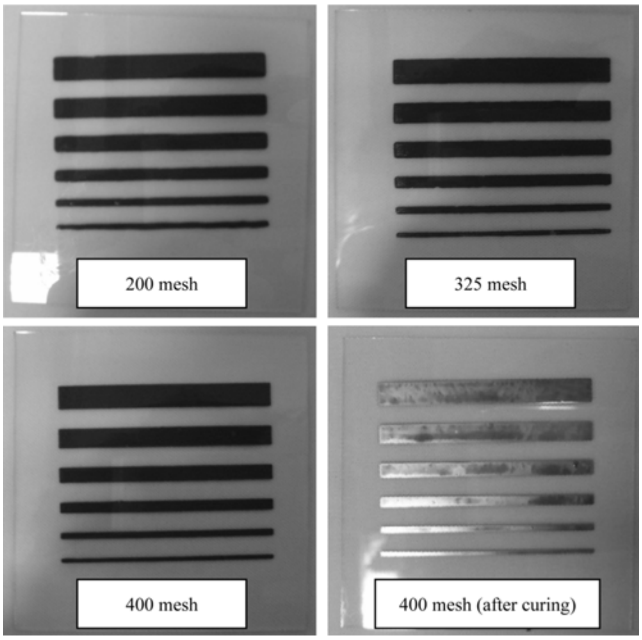

Fig. 3. Photographs of screen-printed silver metal lines printed by using inks with three different mesh counts' screens. The final photograph shows the image after heat treatment at 200 ºC for 5 min.

metal lines printed by using different screen masks are shown in Fig. 3. As shown in the figure, all the lines are found continuous and uniform, but the lines printed with 400 mesh-counts' screen look sharper in the line edges. After heat treatment of the printed lines at a moderate temperature for a certain time, the lines become optically reflective and electrically conductive as a result of the sintering effect.

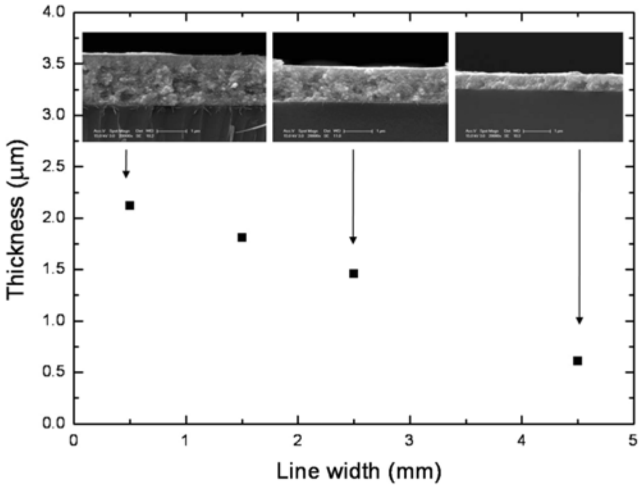

Fig. 4. Dependence of the thickness of screen-printed silver lines on line width measured by SEM.

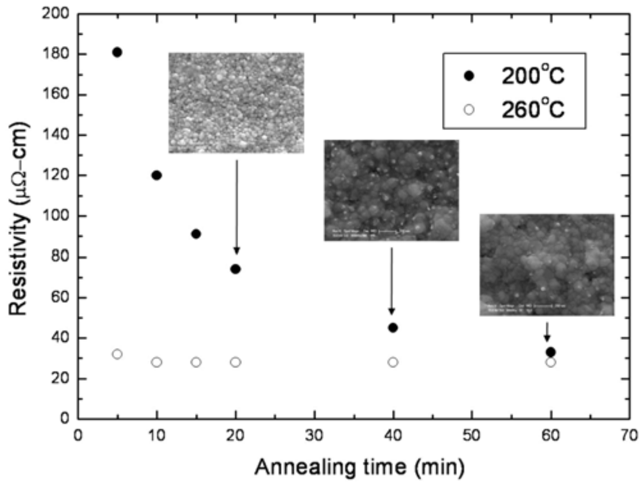

Fig. 5. Electrical resistivity after heat treatment at two different temperatures for various times (line width is 0.5 mm for these data.).

The thickness of the screen-printed lines was measured by SEM and the results are shown in Fig. 4. It shows a monotonic decrease of the thickness with the increase of the line width from 0.5 to 4.5 mm. Before the thickness was measured, the printed lines were baked at a temperature of 200 ºC for 5 min. Theoretically, the thickness should be constant regardless of the line width since the same mesh screen has been used. We could attribute this result to the fact that the edges of the printed lines should be thicker than the center of the lines due to the emulsion thickness of the patterned screen. Because of the thicker edges, the resulting line thickness was thicker for the narrower line width after reflow of the lines at the sintering temperature.

An electrical furnace was used to treat the screen-printed silver lines to remove the solvent and to cause the sintering effect between nanosized silver particles. The electrical resistances of these lines after curing are shown in Fig. 5 as a function of time at two different curing temperatures. Generally, the resistance should decrease with curing time at a constant temperature, as a result of the sintering effect for nanosized silver particles. As shown in the figure, while the sintering for 5 min at 260 °C is almost sufficient to form conductive silver lines, a prolonged sintering time of 60 minutes is needed to have the silver lines with the same resistivity at the 200 °C curing temperature. In that the electrical resistivity of bulk silver is 1.51 μΩ·cm, the resistivity of silver lines of about 30 μΩ·cm is 20 times higher than the lowest. We consider that the resistivity is enough to serve as conducting lines for electronic applications. Fig. 5 also shows the SEM images of surface morphology after curing the printed lines for different times at a temperature of 200 °C. Here one can easily notice the sintering effect with time. At 200 °C for 20 min, each silver particle seems to be unchanged and can be clearly observed. After 40 min curing, boundaries between particles start to disappear due to sintering and consequently the electrical resistance decreases. After 60 min most boundaries disappear and the electrical resistance decreases to a lower value.

CONCLUSIONS

Nanosized silver colloids were synthesized by chemical reduction with formaldehyde and then dispersed in a co-solvent system consisting of diethylene glycol and de-ioned water to make silver screen-printing ink. This work shows that 60 wt.% silver ink is enough to result in uniform and continuous silver lines for screen printing with 400 mesh counts' screen. For a line with the width of 0.5 mm, the thickness of printed line was measured to be 2.12 μm and the electrical resistivity was 33 μΩ·cm after heat treatment at 200° C for 60 min. Compared with the bulk resistivity of silver (1.51 μΩ·cm), the resistivity of the screen-printed silver line was found to be an order of magnitude higher, but it could be considered to be in the range for serving as conducting lines for electronic applications.

ACKNOWLEDGMENTS

This work was supported by Grant No. (R01-2006-000-10140-0) from the Basic Research Program of the Korea Science & Engineering Foundation. It was also partly supported by the Advanced Materials Process Research Center for IT at Sungkyunkwan University.

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