

Silver complex inks for ink-jet printing: the synthesis and conversion to a metallic particulate ink

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A solution ink of a silver complex was prepared by dissolving silver neodecanoate in xylene up to a concentration of 25% silver (Ag-SI). Spun-coated Ag-SI films were thermally decomposed to metallic silver films with resistivity values of less than $4.5 \times 10^{-5} \Omega \cdot \text{cm}$, after sintering above 160°C. In addition, a silver nanoparticle ink (Ag-PI) could be prepared by removing a large amount of neodecanoic acid from the Ag-SI by reduction with phenylhydrazine. The sintering temperature for Ag-PI with a resistivity below $1 \times 10^{-4} \Omega \cdot \text{cm}$ was reduced from 160°C to 130°C by using Ag-PI instead of Ag-SI. However, Ag-PI was rather unstable, as a precipitation occurred in one week at room temperature. Finally, Ag-SI was tested for production of a metallic film on a polyamide as a metal complex ink in a drop-on-demand ink jet printer. The results indicated that it would be very suitable as a conducting ink.

Key words: Ink jet printing, Silver solution ink, Silver nanoparticle ink.

Introduction

The ink jet printing process has been used as a direct patterning method where the desired pattern was formed by ejecting very small droplets of ink through a nozzle onto a substrate. Ink jet printing is a very simple and economic method compared to conventional patterning processes such as photo-lithography. Therefore, ink jet printing using various inks composed of metals, semiconductors, polymers, and organics has been intensively researched for micrometer-ordered patterning in various electronic applications including flat panel displays (FPD), semiconductor packaging, photovoltaic cells, and micro-electromechanical systems (MEMS) [1].

Silver nanoparticle ink (SNI) for ink-jet printing has been also thoroughly investigated for use in the production of electrode or circuit patterns in plasma displays (PDP), radio frequency identification (RFID), and photovoltaic solar cells [2-4]. Silver nanoparticles in SNI must be stable against agglomeration and grain growth; otherwise, clogging in the ink jet head may result. Also, SNI of a sufficiently high concentration is desirable to obtain the desired conductivity of the patterns at a relatively low sintering temperature.

Furusawa et al. [5] fabricated silver bus electrodes for a plasma display with an SNI that contains silver nanoparticles (average size of 3.8 nm) in an organic

solvent of low volatility. Magdassi et al. [6] prepared an aqueous SNI with a stabilizer of carboxymethyl-cellulose and applied it to ink jet printing on paper and transparencies. However, silver nanoparticles are generally unstable and tend to grow larger, even in the presence of polymeric stabilizers, especially at high solid contents. Magdassi et al. [6] also reported that the average particle size of a silver nanoparticle hydrosol stabilized by carboxymethyl-cellulose increased from 40-70 nm to 90-120 nm after seven months of storage. Li et al. [7] observed that silver nano-particles with a size range of 10 to 40 nm grew to about 200 nm after aging the colloid at ambient temperature for three months even though dodecylbenzene sulfate was present as a stabilizer.

On the other hand, silver solution ink, where a silver complex is dissolved in a solvent and can be thermally decomposed to metallic silver after the patterning process, has been reported. Because the silver complex ink is very stable, even at concentrations up to saturation, neither additional stabilizers nor reducing agents are required. Teng and Vest [4] prepared a silver solution ink by dissolving silver neodecanoate in xylene, which is stable up to 20 wt% of silver. They patterned collector grids on silicon wafers for photovoltaic solar cells with the ink by using the ink jet printing method. Dearden et al. also used a silver neodecanoate solution as an ink for a drop-on-demand type ink-jet printing [8]. Recently, Wu et al. reported that a conductive silver electrode in a printed thin-film transistor (TFT) was formed by a spin coating method with a silver complex solution in which silver acetate was dissolved

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in butanol with ethanolamine [9].

In this study, we prepared two kinds of inks (Ag-SI and Ag-PI): silver solution ink (Ag-SI) was prepared by dispersing silver neodecanoate in xylene and Ag-SI was reduced with a weak reductant into the silver nanoparticle ink (Ag-PI). The effect of curing temperature on the resistivity of the spun-coated films was investigated for both inks. In addition, Ag-SI was tested to produce a metallic film on a polyamide as a metal complex ink in a drop-on-demand ink jet printer.

Experimental Procedure

An amount of 8.613 g of neodecanoic acid (technical grade, Strem Chemicals, Newburyport, MA, US) was dissolved in 20 ml of aqueous NH_4OH solution (3.15 ml, 30%, Samchun Chemical Co. Ltd., Pyungtaek, Korea) and 8.494 g of silver nitrate (99.9%, Kojima Chemicals Co., LTD. Japan) was dissolved in 20 ml of distilled-deionized water. A white precipitate of silver neodecanoate ($\text{AgCOOC}_9\text{H}_{23}$) was rapidly produced by mixing the two solutions.

After filtration and washing with deionized water, the sticky precipitate was redispersed in 200 ml of ethanol (95%, Samchun Chemical Co. Ltd., Pyungtaek, Korea) with vigorous stirring for 3 h. The resulting white suspension of silver neodecanoate was again filtered and washed with ethanol and acetone. The silver neodecanoate powders obtained were dissolved in toluene to prepare the Ag-solution ink (Ag-SI, 25 wt% silver).

For a silver nanoparticle ink, 0.98 ml of phenylhydrazine (97%, Aldrich, NJ) was dissolved in 100 ml of toluene and slowly added to the toluene solution of silver neodecanoate. After stirring at room temperature for 1 h, a stable dark brown colloid, indicating the formation of silver nanoparticles, was obtained. Excess amounts of acetone and methanol (95%, Samchun Chemical Co. Ltd., Pyungtaek, Korea) were poured into the colloid to sediment the silver nanoparticles. After decanting, the resulting suspension was filtered, washed with methanol 3 times, and dried in a vacuum oven at 30°C for 12 h. The silver nanoparticles obtained were dispersed again in toluene to prepare an Ag-nanoparticle ink (Ag-PI, 25 wt% silver).

Silver films were formed on polyimide (PI) substrates by a spin-coating method with Ag-SI and Ag-PI. The spin coating was conducted in two stages: 1000 rpm for 10 s and 3000 rpm for 30 s. Ag-SI was also tested for ink jet printing with a drop-on-demand (DOD) ink-jet head (OmniDot 380, Xaar, U.K.). Various silver patterns were formed on polyimide films by the head filled with 25% Ag-SI ink. The formed patterns were sintered at 230°C for 1 minute.

Thermogravimetric analysis (SDT 2960, TA Instruments, New Castle, DE, US) was conducted under air at a heating rate of $10 \text{ K} \cdot \text{minute}^{-1}$. The crystallographic structure of the Ag nanoparticles was determined by an

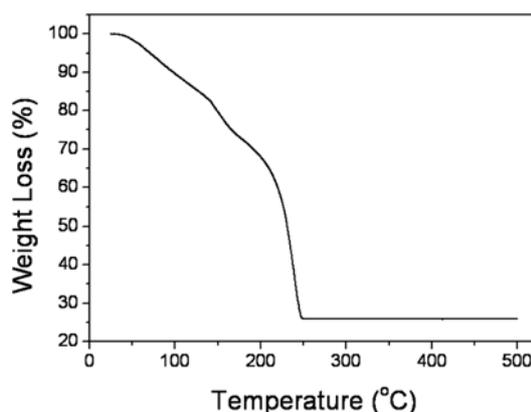


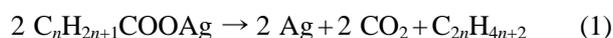
Fig. 1. TGA curve for silver neodecanoate solution ink (Ag-SI, 25% of silver).

XRD (X-ray diffractometer, Rint-2000, Rigaku, Tokyo, Japan) using $\text{Cu-K}\alpha$ radiation at 40 kV and 100 mA. The size and morphology of Ag nanoparticles were observed by TEM (transmission electron microscopy, JEM-2000 EXII, Jeol, Tokyo, Japan). The surfaces and cross-sections of the spun-coated films and ink jet patterns were investigated by SEM (scanning electron microscopy, Model JSM-2010, Jeol, Tokyo, Japan). The electrical conductivity of the films was measured by a four-point probe (CMT-SR2000N, Jandel, U.K.) technique.

Results and Discussion

Although silver carboxylates (Ag-COOR) are widely known as good precursors for silver nanoparticles by thermal reduction at low temperatures [10-14], most silver carboxylates have poor solubility in organic solvents, due to their structure. Binnemanns et al. [14] proposed that silver carboxylates had a highly ordered structure with repeating $[\text{Ag}(\text{C}_n\text{H}_{2n+1}\text{COO})]_2$ dimer units, which was confirmed from well-defined XRD peaks at low diffraction angles. Silver neodecanoate exhibited good solubility in some organic solvents such as toluene and xylene as reported by Teng and Vest [4] and Dearden et al. [8]. It is considered that the high solubility of silver neodecanoate originates from its poorly ordered structure with branching alkyl groups at alpha carbon positions in neodecanoic acid ligands.

Figure 1 shows the TGA curve for the xylene solution of silver neodecanoate (25%, Ag-SI). As can be seen in Fig. 1, the thermal reduction of Ag-SI into metallic silver was initiated at around 140 in air even though Ag-SI became pure metallic silver at 230°C . Although the exact mechanism for thermal decomposition of silver carboxylates is not fully understood, the following mechanisms have been proposed [14, 15]:



Therefore, it was considered that the change in the slope of the weight loss at around 140°C in Fig. 1 correlated with the evolution of CO₂ gas and reduction of silver. The formation of metallic silver particles from Ag-SI at temperatures lower than 230°C was also confirmed by the SEM analysis. Figure 2 shows the SEM images for the spun-coated films of Ag-SI at various sintering temperatures. It can be seen that fine silver particles were formed even at 150°C, then grew to larger particles and fused by necking at the higher temperature.

The variation of resistivity for the Ag-SI films on sintering temperatures was also investigated. As shown in Fig. 3, sheet resistance decreased to below 1.496 Ω/sq. when the film was sintered at temperatures greater than 160°C. Considering the film thicknesses were about 150 to 300 nm, which was confirmed by SEM analysis, they had a resistivity less than 4.5×10^{-5} Ω·cm. Therefore, the Ag-SI films had a resistivity of the order of 10^{-6} Ω·cm when sintered above 190°C.

On the other hand, Li et al. [16] found that sintering at a temperature lower than 160°C is necessary for the

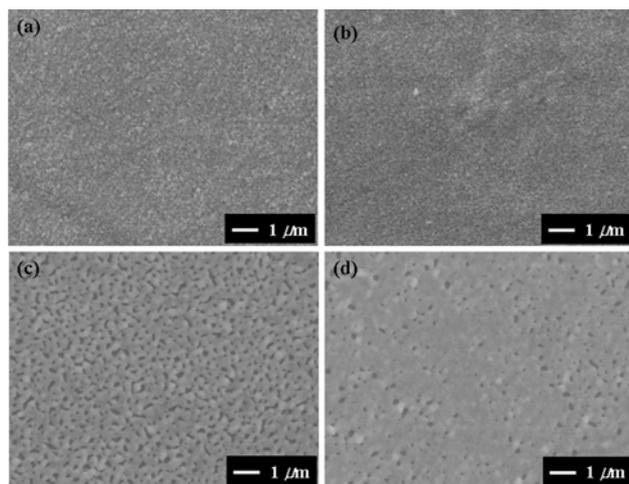


Fig. 2. SEM images of Ag-SI films sintered at various temperatures: (a) 150°C, (b) 170°C, (c) 200°C, and (d) 220°C.

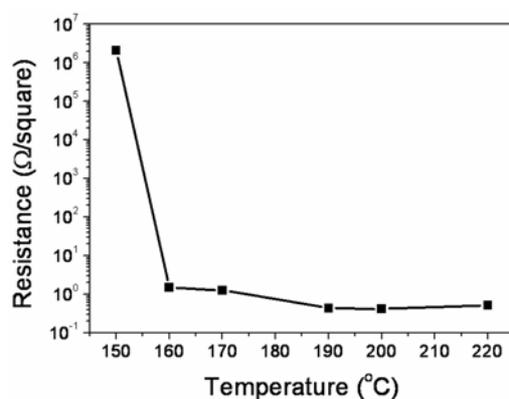


Fig. 3. Variations of the Ag-SI film's sheet resistance depending on the sintering temperature. The time at each temperature was 10 minutes.

silver ink to be compatible with plastic substrates for flexible electronics. Therefore, in order to meet the requirement that the film resistivity should be under 10^{-5} Ω·cm at a sintering temperature lower than 160°C, a silver nanoparticle ink (Ag-PI) was developed. The synthetic procedure for Ag-PI is as follows; 1) Ag-SI was reduced to silver nanoparticles with a weak reductant of phenylhydrazine, 2) most of the liberated neodecanoic acid was removed by washing and filtering, and 3) the resulting nanoparticles were redispersed in xylene to create the Ag-PI ink. The silver nanoparticles in Ag-PI were well dispersed in xylene up to 20%, owing to the fact that the adsorbed neodecanoic acid on the surfaces of the silver nanoparticles remained even after washing and acted as a stabilizer [11]. The TGA curve of Fig. 4 shows that the residual neodecanoic acid on the silver nanoparticles is about 17%.

The formation of the silver nanoparticles from Ag-SI was confirmed by TEM and XRD analyses (Fig. 5). The broad XRD peaks centered at 2θ of 38.1, 44.3, and 64.4° corresponded with (110), (200), and (220) lattice planes of face-centered cubic silver, respectively. The average particle size of the silver nanoparticles was 4.9 nm with a standard deviation of 2.3 nm. Ag-PI films were prepar-

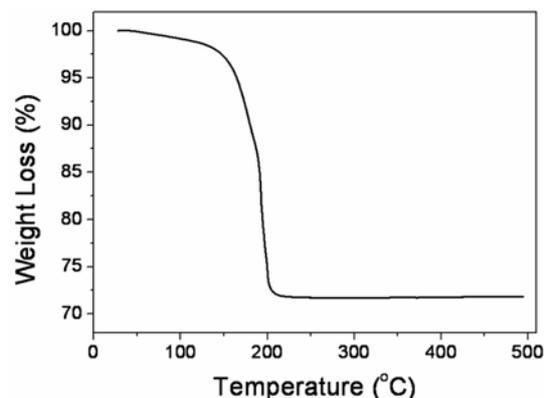


Fig. 4. TGA curve for the silver nanoparticles prepared by reducing Ag-SI with phenylhydrazine.

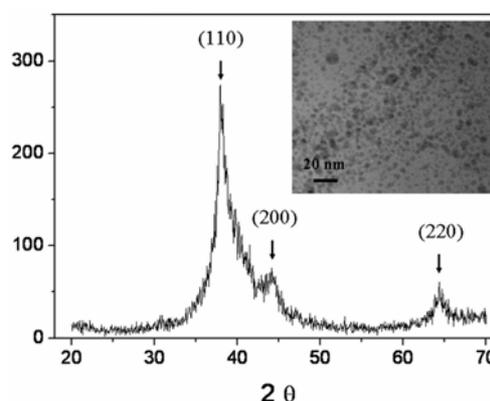


Fig. 5. The XRD pattern of the silver nanoparticles obtained by reducing Ag-SI with phenylhydrazine. The inset is a TEM image of the silver nanoparticles.

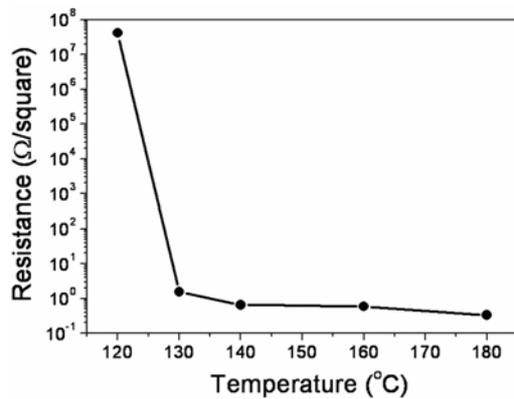


Fig. 6. Variations of the sheet resistance of the Ag-PI films depending on sintering temperature. The time at each temperature was 10 minutes.

ed by a spin-coating method and the resistivity, as it depended on the sintering temperature, was investigated (Fig. 6). The temperature at which the sheet resistance decreased below $1.534 \Omega/\text{sq.}$ was 130°C , which was 30 lower than that of Ag-SI.

Li et al. [16] observed that the sintering temperature for a film with a desired conductivity could be lowered more by using silver nanoparticles with a shorter chain alkylamine as a stabilizer than by using other stabilizers such as carboxylates, ammonium salts, polymers, or long chain alkylamines. They attributed the lower sintering temperature to a weak interaction of the alkylamine with metal atoms such as silver, while other stabilizers interacted strongly with metal atoms, making removal difficult at low sintering temperatures. By contrast, in our study, Ag-PI exhibited a low sintering temperature of 130°C although it contained a carboxylic acid as a stabilizer. Because most of the stabilizer was removed by the washing steps, we presume that the amount of residual stabilizer was small enough to easily decompose, facilitating the grain growth of silver particles with neighboring ones at a relatively low sintering temperature.

Although Ag-PI films had a low sheet resistance of $1.534 \Omega/\text{sq.}$ after sintering at 130°C for 10 minutes, Ag-PI ink exhibited a colloidal stability problem, precipitating at room temperature within one week. Due to its insatiability, ink jet printing was conducted only with the Ag-SI ink. The Ag-SI patterns were prepared on polyimide films using a drop-on demand ink-jet printer and sintered at 230°C for 1 minute. Various silver patterns with the narrowest line width of $\sim 210 \mu\text{m}$ and spacing width of $\sim 120 \mu\text{m}$ were successfully formed, as shown in Fig. 7. They exhibited a low sheet resistance of $0.17 \Omega/\text{sq.}$ with a thickness of 367 nm (resistivity of $6.24 \times 10^{-6} \Omega \cdot \text{cm}$) and good adhesion property with the substrates, while showing high stability. Therefore, Ag-SI appears to be a suitable ink for forming various silver patterns by ink jet printing for printable electronics (Fig. 8).

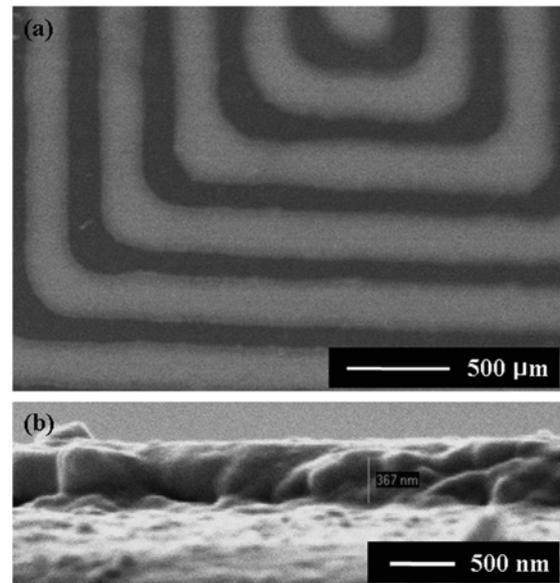


Fig. 7. SEM images for the (a) surface and (b) cross-section of an inkjet-printed silver pattern.

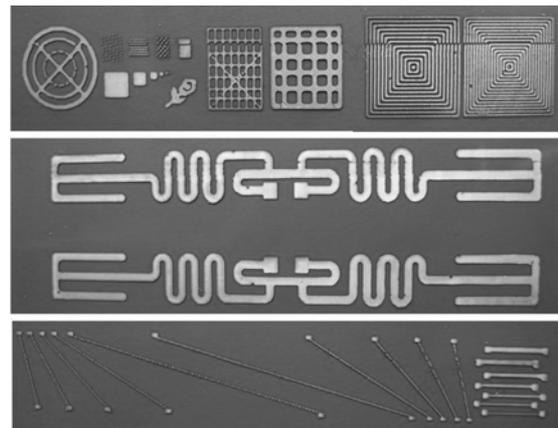


Fig. 8. Various silver patterns formed by ink-jet printing with the Ag-SI ink.

Conclusions

Two types of silver ink (Ag-SI and Ag-PI) for ink jet printing were prepared: 1) Ag-SI was prepared as a xylene solution of silver-neodecanoate (25% silver) and 2) Ag-PI was prepared by reducing Ag-SI with phenylhydrazine and then redispersing in xylene (20% silver). Because Ag-SI was a true solution ink, it exhibited better stability than did Ag-PI, while Ag-PI had a relatively lower sintering temperature of 130°C with a resistivity value of $1 \times 10^{-4} \Omega \cdot \text{cm}$ compared to Ag-SI, which had a resistivity of $4.5 \times 10^{-5} \Omega \cdot \text{cm}$ after sintering at temperatures above 160°C . By applying Ag-SI to ink jet printing with drop-on-demand type heads, various types of patterns with narrow line widths and spacing widths could be prepared.

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