Stepwise current electrical sintering method for inkjet-printed conductive ink

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Stepwise current electrical sintering method for inkjet-printed conductive ink

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An innovative electrical current sintering technique is applied to joule-heat conductive ink by increasing current gradually through a stepwise-form. This stepwise electrical sintering technique is devised to overcome thermal damage of printed conductive ink line during electrical sintering due to its high initial resistance. To monitor a stepwise electrical sintering method, in-situ specific resistance was measured. Surface morphology of the sample was observed by field-emission scanning electron microscope. By increasing the current gradually, the conductive line can endure higher current because the specific resistance has dropped gradually during the process. Finally, enhanced final-step current produces lower specific resistance of the conductive line than that obtained from a constant current-supplying electrical sintering method without damaging printed conductive line.

1. Introduction

As a technology of printed electronics emerges, a new method for high productivity of electronic devices to meet the increasing demand has been requested recently. Lithography and etching, which are typical conventional patterning methods, have some cons: They need complex processes including chemical treatment and high-vacuum-process and produce material waste, resulting in heavy environmental load.[1] As an alternative to the lithography and etching methods, inkjet-printed electronics have drawn attention. The inkjet-printing method needs only simple processing steps: printing and sintering. Electronic devices can be made in ambient environment through inkjet-printing method. To manufacture the electronic devices, metal nanoparticle ink is used in inkjet-printing method.[2] Metal nanoparticle ink was separated by the solvent to prevent the nozzle clogging caused by agglomeration due to van der Waals force. The separated nanoparticle inks by solvent have high initial resistance.[3] Silver nanoparticles generally need a heat treatment process to improve their electrical conductivity after being printed on substrate. To sinter the conductive ink, furnace and hot plate methods are usually adopted to heat up the whole substrate for more than 30 min. However, the high sintering temperature can damage thermally sensitive substrate such as glass, polyethylene terephthalate, and paper.[1] To reduce substrate damage, the electrical sintering which can selectively heat up the conductive ink lines is attractive.

Thermal damage of conductive ink line can occur during the electrical constant current sintering caused by high initial resistance of the conductive ink line.[4] An innovative electrical current sintering technique is devised to overcome the thermal damage of printed conductive ink due to initial high resistance by increasing current gradually through a stepwise-form. By increasing the current gradually, the conductive line can endure higher current because the specific resistance has dropped gradually during the process. Finally, maximum final-step current causes lower specific resistance of the conductive line than that obtained from constant-current electrical sintering method without damaging printed conductive lines.

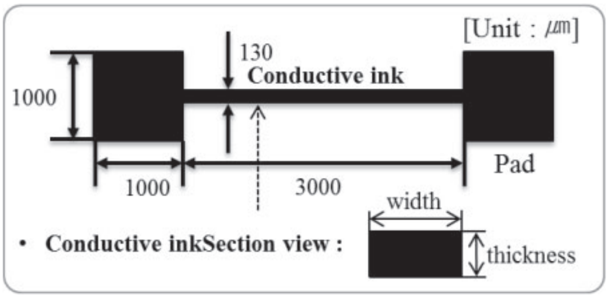

Fig. 1. Pattern shape of the ink-jet-printed conductive line.

To monitor a stepwise electrical sintering method, in-situ specific resistance was measured. Surface morphology change of s sample at each step was observed by field-emission scanning electron microscope.

2. Experiment

2.1 Sample preparation

A commercial silver nanoparticle-ink used in this work consists of 34 wt% silver nanoparticles with an average size of approximately 50 nm. The silver nanoparticles were separated by triethylene glycol monoethyl ether (TGME). The viscosity of TGME was 2–16 cP. Before printing on Eagle-XG (Samsung-Corning) glass substrate, the cleaning process of the substrates was performed. The substrates were cleaned by acetone and isopropyl alcohol solution with an ultrasonic cleaner for 20 min each. The glass substrates were then baked in a furnace at 250 °C for 20 min to eliminate extra moisture on the substrate.

Figure 1 shows the pattern of printed ink. Two pads were printed on the substrate to measure the resistance of conductive lines by DMP-2831 inkjet printer (Dimatix). To reduce initial resistance of pads, the patterned pads were then baked in a furnace at 250 °C for 30 min before printing conductive line pattern. A single droplet volume and ejected drop velocity of the ink were approximately 10 pl and 5 m/s, respectively. The size of patterned conductive ink line was around $3000 \times 130 \times 0.36\ \mu m^3$ (length × width × thickness)

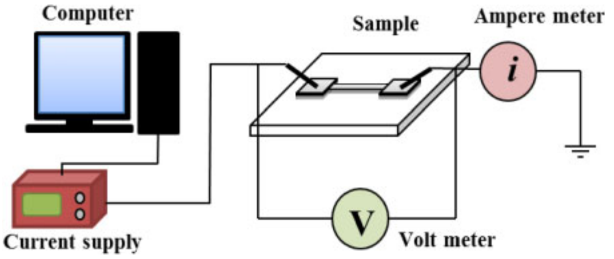

Fig. 2. (Color online) Schematic diagram of the electrical circuit.

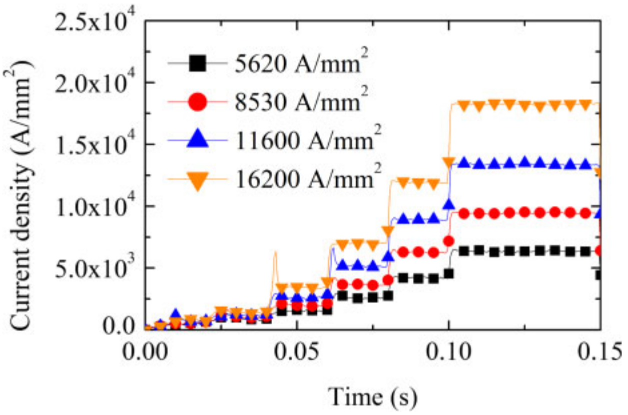

Fig. 3. (Color online) Transient applied current density by stepwise constant current method.

and the pad size was $1000 \times 1000\,\mu m^2$. The resistances of the samples were measured as $1000 \pm 115\,\Omega$.

2.2 Experiments

The schematic diagram of experimental circuit setup is shown in Fig. 2. To measure the current supplying to the circuit, a connecting resistor ($1\,\Omega$) in series with printed sample was adopted during electrical sintering. By connecting four probes to both ends of a sample and a resistor respectively, the in-situ voltage was measured by an oscilloscope to obtain the transient resistance of the ink. Specific resistance was calculated by Ohm's law, as shown below:

$$\rho = R\frac{A}{L}, \tag{1}$$

where ρ, R, A, and L are the specific resistance, line resistance, cross-sectional area, and length of conductive line, respectively. Constant current densities increased gradually depending on time intervals as presented in Fig. 3. The current density was estimated with cross-sectional area measurement after stepwise current sintering. With the measured areas, the estimated final current densities were 5620, 8530, 11600, and $16200\,A/mm^2$, respectively.

2.3 Electrical sintering

The samples were sintered by joule-heating the silver nanoparticles in the printed ink. The equation of joule heating law is as follows:

$$P = VI = I^2R, \tag{2}$$

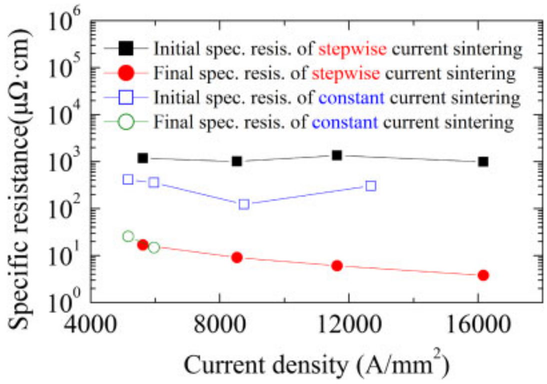

Fig. 4. (Color online) Final and initial resistance with stepwise current sintering and constant current sintering method.

where P, R, I, and V are power, resistance, current, and voltage, respectively. By applying the potential difference to the both ends of the circuit, electrical power is generated and it accelerates the free electrons to move through in the conductive ink line. Moving free electrons collided with silver nanoparticles in the conductive inks and collisional energy was then changed to thermal energy. The thermal energy was caused by joule heating in the sample.[5,6]

3. Results and discussion

Figure 4 shows the final and initial resistances with stepwise current sintering and constant current sintering methods. When the conductive ink line was electrically sintered with a constant current, it was broken over an applied current density of $9000\,A/mm^2$. The minimum specific resistance of the constant current method was $14.9\,\mu\Omega{\cdot}cm$ with a final current density of $5960\,A/mm^2$. It was 9.3 times higher than that of bulk silver ($1.6\,\mu\Omega{\cdot}cm$) at room temperature. The stepwise current sintering method could sinter the conductive ink by over the $5960\,A/mm^2$ at higher initial specific resistance than that of constant current method. By using stepwise current method, the specific resistance of the conductive ink could decrease more. This low specific resistance could improve the performance of electrical device. The minimum specific resistance of the stepwise current sintering method was $3.8\,\mu\Omega{\cdot}cm$, which was 2.4 times higher than that of bulk silver ($1.6\,\mu\Omega{\cdot}cm$). This value was 3.9 times lower than that ($14.9\,\mu\Omega{\cdot}cm$) obtained from constant current method. As shown in Fig. 4, the conductive ink line could endure the high current density with stepwise current sintering method due to lowered resistance of the printed line.

To monitor the stepwise current sintering method, the transient specific resistance was observed. Transient specific resistances of the stepwise current sintering were shown in Fig. 5. The transient specific resistance of the stepwise current method decreased gradually in a stepwise form. Stepwise sintering method can sinter printed samples without damage with a final current density of $16200\,A/mm^2$. The lowest specific resistance at room temperature was $3.8\,\mu\Omega{\cdot}cm$, which was 2.4 times greater than that of bulk silver ($1.6\,\mu\Omega{\cdot}cm$). The transient specific resistance decreased as the applied current density increased.

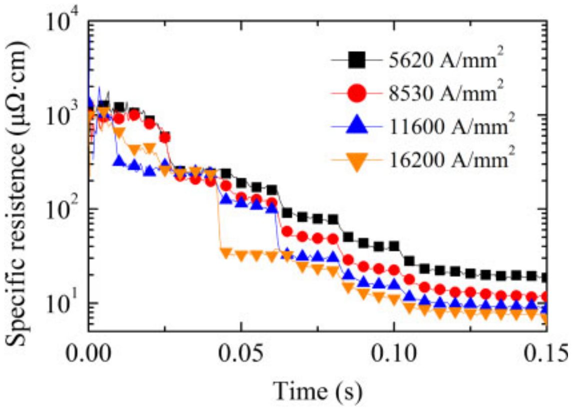

Fig. 5. (Color online) Transient specific resistance of the silver nanoparticle ink during stepwise current sintering method with various applied currents.

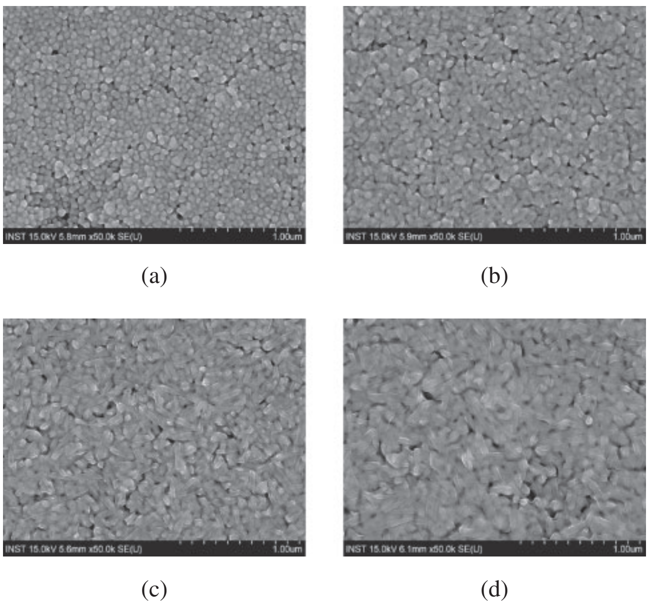

Fig. 6. FESEM image of conductive ink line by stepwise current sintering at 0.15 s: (a) 17.0 μΩ·cm, 5620 A/mm^2, (b) 9.14 μΩ·cm, 8530 A/mm^2, (c) 6.08 μΩ·cm, 11600 A/mm^2, and (d) 3.82 μΩ·cm, 16200 A/mm^2.

Surface morphology changes sintered by stepwise current method for 0.15 s were observed by field emission scanning electron microscope images as shown in Fig. 6. During the sintering process, the solvents among the nanoparticles are rapidly removed and nanoparticles connect each other. The diffusion processes such as surface diffusion, grain boundary diffusion, volume diffusion, and lattice diffusion occur among the particles. These kinds of diffusions make necks among nanoparticles. As increasing the necks among the particles, percolation networks which are in the form of rods, are randomly generated to provide paths for electron flow. With the electrons moved among the particles more freely, specific resistance decreases.[2,7–9] The necks among nanoparticles are hardly discernible in Fig. 6(a). However, as raising the supplied current density, a number of necks increase remarkably. After 11600 A/mm^2, long percolation network was formed unlike other sintering methods such as the furnace sintering and the laser sintering. It might be characteristic of stepwise electrical sintering. The stepwise electrical sintering could apply the high current density in a short time. As the electrons passed along electron path during the electrical sintering process, heat transfer also mainly occurred through this path. This phenomenon might drive the mass transfer along the electron passages. As a result, the percolation networks were noticeably formed under the stepwise current sintering method. This trend was remarkably shown as increasing the applied current density in Figs. 6(b) and 6(c). Above the 16200 A/mm^2, the percolation networks were then agglomerated together as shown in Fig. 6(d). As changing surface morphology, the specific resistance of the printed line measured at room temperature decreases. It shows that specific resistance remarkably decreases as the necks grow densely among Ag nanoparticles. However, the obtained specific resistance is higher than of that of bulk silver. It might be caused by the existence of voids in the conductive line as shown in Figs. 6(c) and 6(d).[10]

4. Conclusion

By increasing the current at regular time intervals in a stepwise form, the conductive line could endure higher current because the transient specific resistance had gradually dropped during the process. The stepwise constant current sintering method could avoid damage caused by high initial resistance of the printed line. The necks among the silver nanoparticles formed percolation network above 11630 A/mm^2 current density. The specific resistance of the conductive ink decreases because of the formation of percolation network, neck growth, and the condensation of necks.

Acknowledgments

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