# Silver Conductive Features on Flexible Substrates from a Thermally Accelerated Chain Reaction at Low Sintering Temperatures

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ABSTRACT: In this study, a simple and effective silver ink formulation was developed to generate silver tracks with high electrical conductivity on flexible substrates at low sintering temperatures. Diethanolamine (DEA), a self-oxidizing compound at moderate temperatures, was mixed with a silver ammonia solution to form a clear and stable solution. After inkjet-printed or pen-written on plastic sheets, DEA in the silver ink decomposes at temperatures higher than 50 °C and generates formaldehyde, which reacts spontaneously with silver ammonia ions to form silver thin films. The electrical conductivity of the inkjet-printed silver films can be 26% of the bulk silver after heating at 75 °C for 20 min and show great adhesion on plastic sheets.

KEYWORDS: chain reaction, silver ink, low sintering temperature, silver thin film, inkjet printing, conductive tracks
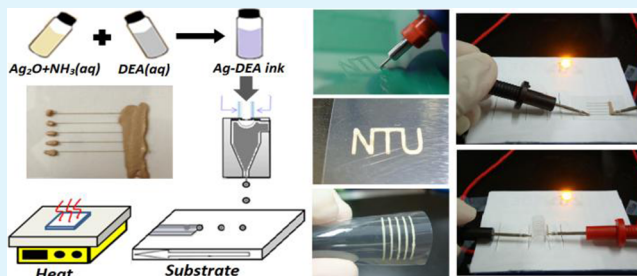
■ INTRODUCTION

Recently, substantial attention has been paid to developing printing technologies for flexible electronic devices, such as a flexible display,[1,2] solar cell arrays,[3,4] and radio-frequency identification (RFID).[5-7] Instead of conventional lithography technology, those so-called printed electronics make use of various printing methods to transfer inks on flexible substrates to create conductive or semiconductive thin-film patterns with fast speed and low cost. To connect the electronic parts in the printed devices, solution-based inks are printed and transformed into conductive metal tracks after a thermal post-treatment. To obtain interconnects between electronic elements with high conductivity, silver, the metal with the lowest resistivity, is commonly used for printed conductive tracks. Commonly used silver nanoparticle inks generally need a high-temperature sintering process to enhance the electric conductivity of printed tracks. Regularly, a sintering process at temperatures of around 150−250 °C for 1−2 h is required to remove electrically nonconductive organic components in the ink, and the electrical conductivity of printed tracks can be enhanced to 20−30% of bulk silver.[8-12] Because of the thermoplastic nature of plastic flexible substrates, the high sintering temperature of silver inks restricts the choice of substrates. To lower the ink sintering temperatures on plastic substrates, researchers have tried to make use of other sintering processes, such as microwave,[7] laser curing,[5] plasma treatment,[12] reactive inkjet,[13] and UV curing.[14,15]

Although the aforementioned alternative methods have given fruitful and plausible results, thermal post-treatment is still extensively used in the printing of commercial silver inks because of its wide availability and easy access. To reduce the ink sintering temperatures for conductive features, various approaches have been proposed in the literature to formulate silver salt complex solutions[16,17] with low sintering temperatures of around 90−110 °C. After printing and thermal post-treatments, the organic silver complex decomposes and can be transformed into highly conductive silver thin films close to bulk silver. However, the organic salt formulation processes are usually quite complicated and require several synthetic steps. On the other hand, in the literature, silver nanoparticles or thin films are generally synthesized from redox reactions of silver ions and reducing agents, such as ethylene glycol,[16] polymers [such as poly(vinylpyrrolidine) (PVP)],[18-20] or amines,[15] at temperatures ranging from 60 to 100 °C. If silver ions and the reducing agents can coexist in a solution for a long time at room temperature before printing, the as-printed ink can then be heated and generates silver nanoparticles on the printed area to form silver patterns at temperatures below 100 °C. Following this idea, Wu et al.[21,22] formulated a stable silver ink by mixing a mild reduction agent with a silver salt complex to produce conductive silver features (>10^4 S/cm) at a sintering temperature of 150−200 °C after 45 min of annealing.

To produce highly conductive silver thin films at an even lower sintering temperature within a short time, in this article, we make use of a temperature-sensitive reduction agent to formulate a new silver ink. A silver ammonia solution is mixed with diethanolamine (DEA), a self-decomposing compound. This silver ink is a clear aqueous solution and remains transparent for weeks with proper storage. When the ink is heated to temperatures higher than 50 °C,[23] formaldehyde generated from decomposition of DEA reacts quickly with silver ammonium ions and generates highly conductive silver

tracks on plastic substrates. This ink can be used in both inkjet printing and pen-writing technology to generate micropatterns of silver thin films with great adhesion on plastic surfaces after a short period of thermal post-treatment at moderate temperatures.

■ EXPERIMENTS

Flexible poly(ethylene terephthalate) (PET) slides (Universal Films, Japan) of 2.5×2.5 cm^2 were cleaned by rinsing sequentially with deionized (DI) water and ethanol in an ultrasonic bath (Delta DC300H) and were dried in a vacuum oven. The silver ammonia solution was prepared by adding 0.3 g of silver oxide (Alfa Aesar, USA) to a solution of 1 mL of DI water and 4 mL of ammonium hydroxide (33%, Sigma Aldrich, USA). The DEA aqueous solution was prepared by adding 3.15 g of DEA (Sigma Aldrich, USA) to 1.85 g of DI water. After these two solutions were mixed with various volume ratios (Table 1), the resulting mixture was filtered with a 0.45 μm filter

**Table 1. Properties of Inks at Various Ag$^+$/DEA Ratios**

ink (Ag$^+$/DEA)	viscosity (cP)	surface tension (mN/m)	contact angle (deg)	pH	stable[a]
2:1	2.45	53.2	30	14.5	N
1:1	4.4	49.2	30	14.0	Y
1:2	7.5	48.7	40	13.8	Y

[a]Without UV−vis absorption peaks at 370 nm within 24 h.

(Advantec HP045AN) to remove airborne particles. The ink viscosities were measured by a Brookfield DV-III ultrarheometer at 20 °C. The surface tensions and contact angles of the resulting inks were both measured by standard drop analysis with an in-house goniometer. The weight loss of the silver ink was analyzed with a TA Instrument thermogravimetric analyzer 2050 at a heating rate of 10 °C/min. Drop deposition was made by a MicroFab JetLab4 system (MicroFab Technologies Inc.) with a 50 μm piezoelectric nozzle. Droplets of 50 μm were ejected at a speed of 5 m/s at a frequency of 500 Hz with a dot spacing of 50 μm for printed patterns. Although smaller droplets can be produced at a higher speed with proper printing parameter adjustment, we did not pursue the printing speed or resolution improvement because this study focused mainly on ink formulation and the concept proof of the two-step decomposition/reduction mechanism. The as-printed samples were heated at 75 °C for another 20 min to allow silver reduction and nanoparticle grain growth, and the baked samples were rinsed with DI water to remove unreacted components. The microstructures of printed samples were examined with a scanning electron microscope (Nova NanoSEM 230), and their thickness was determined by an α-stepper surface profilometry (Veeco Dektak 6M). The crystalline structure of the silver films was investigated with an X-ray diffractometer (Rigaku Ultima IV). The sheet resistance or resistivity of synthesized silver thin films was measured with a multimeter (model 2000, Keithley) in four-probe mode.

■ RESULTS AND DISCUSSION

Silver Recovery Process and Ink Formulation. The silver recovery process in the ink is a two-step reaction involving the self-degradation of DEA and silver mirror reaction. Puttaswamy et al.[23] have shown the decomposition of ethanolamines in an alkaline buffer medium at 40 °C as follows:

$$HN(CH_2CH_2OH)_2 + 2OH^- + 2H_2O$$

$$\rightarrow 2HCHO + 2HCOO^- + NH_3 \quad (1)$$
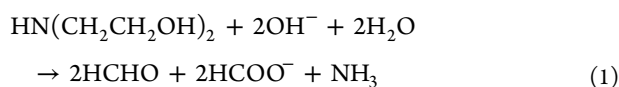
The formaldehyde accompanying with DEA degradation then works as a reduction agent and reacts with the silver ammonia

ions in the inks quickly to form silver nanoparticles, or the so-called silver mirror reaction:

$$HCHO + 2[Ag(NH_3)_2]^+ + 2OH^-$$

$$\rightarrow HCOONH_4 + 2Ag \downarrow + 3NH_3 + H_2O \quad (2)$$
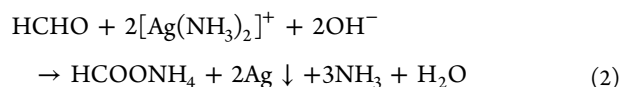
The silver ammonium ions in eq 2 are usually prepared from AgNO$_3$. However, nitrate salts, such as NH$_4$NO$_3$, can be embedded in the silver thin films after ink drying and decrease the conductivity. Thus, to enhance the electrical conductivity, a simplified approach starting from Ag$_2$O and ammonia was used in this study.

$$Ag_2O + 4NH_3 + H_2O \rightarrow 2[Ag(NH_3)_2]^+ + 2OH^- \quad (3)$$
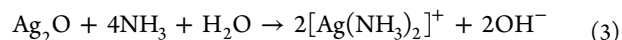
In the serial reaction mechanism for silver nanoparticle formation, as shown in eqs 1 and 2, the DEA decomposition rate at room temperature is fairly slow compared to the silver mirror reaction rate and determines the silver conversion rates. Figure 1 shows the UV−vis spectra of inks stored at various
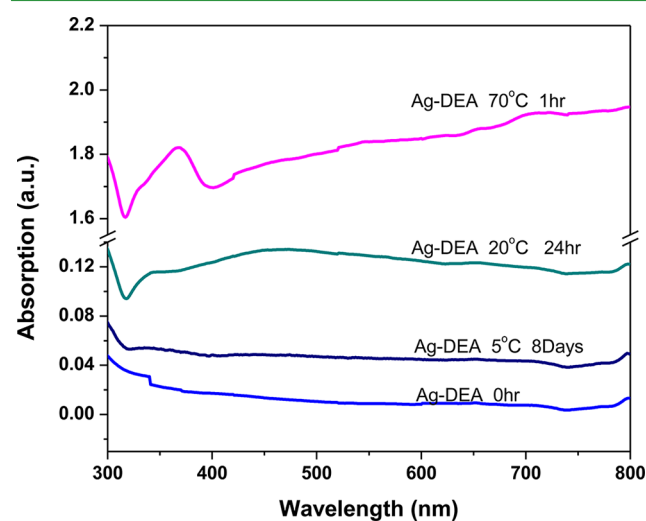
Figure 1. UV spectra of the silver ink stored at various temperatures. The ink contains 30 wt % DEA and 3 wt % silver ammonium.

temperatures. At room temperature, the silver ammonium solution is transparent. After the addition of DEA, the ink is initially transparent without any obvious absorption peaks in the UV−vis spectra. Then, DEA decomposes slowly and generates silver nanoparticles gradually. However, the decomposition is really slow, and the ink turbidity only increases slightly after 24 h. After 3 days, the silver ink becomes cloudy (Figure 2a), and one can observe a small amount of silver nanoparticle aggregates at the bottom of the bottle. The lifetime of the ink can be extended upon storage at lower temperatures. For those inks stored in a refrigerator at 5 °C, DEA decomposition slowed down and thus reduced the generation rates of silver nanoparticles. After 8 days, there was nearly no sign of silver formation in the UV spectrum (Figure 1), and the ink remained visually transparent (Figure 2).

The stability of prepared silver inks is also affected by the pH of the solutions. As mentioned in the literature, DEA decomposes easily in a highly alkaline environment.[23−26] Because the silver ammonium solutions are prepared by saturating Ag$_2$O in a 33% ammonia solution, which has a high pH of 14.8, the direct addition of DEA into an Ag(NH$_3$)$_2$ solution leads to fast silver particle formation. To avoid the fast

(a)

(b)
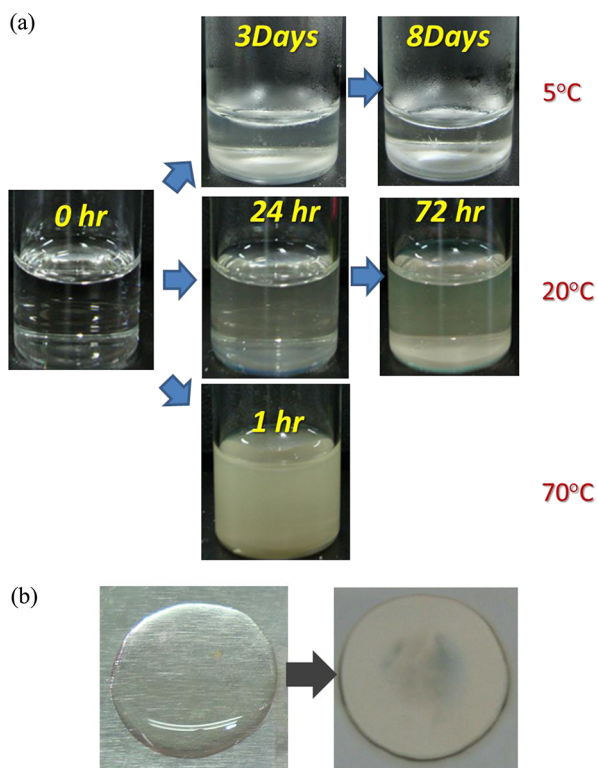
Figure 2. (a) Images of inks stored at 5, 20, and 70 °C. The ink stays transparent for more than 1 week at 5 °C, while visible particle aggregates present in 1 h at 70 °C. (b) Thin-film formation by heating of the ink on the PET substrate at 70 °C for 1 h.

Figure 3. TGA/DTA curves for the silver ink (DEA:Ag$^+$ = 1:1) at an annealing ramping rate of 10 °C/min.

particle formation and increase the storage stability of prepared inks, DEA was first diluted with water and the resulting 63 wt % aqueous DEA solution was then added slowly to the silver ammonium solution. Inks with various $Ag(NH_3)_2$/DEA ratios were prepared to evaluate the time of stable storage. It was found that, for pH values of less than 14 (Table 1), the prepared inks can be stable for more than 24 h at room temperature. To maximize the silver content in the inks, a ratio of 1:1 Ag$^+$/DEA aqueous solutions was used in the following experiments.

The silver recovery process can be accelerated by heating of the silver inks at moderate temperatures. As shown in the pictures in Figure 2a, after immersion in a water bath of 70 °C for 1 h, a large amount of silver nanoparticles was recovered and one can observe gray precipitation at the bottom of the bottle. The UV spectrum of the particle suspension shows a peak at 370 nm, indicating silver nanoparticle formation. This temperature-sensitive particle formation mechanism can be then utilized to create silver thin films (Figure 2b) by heating of a silver ink drop on plastic substrates. The synthesized silver films show great conductivity, and the ink can be used in creating micropatterns with the procedures in the following sections.
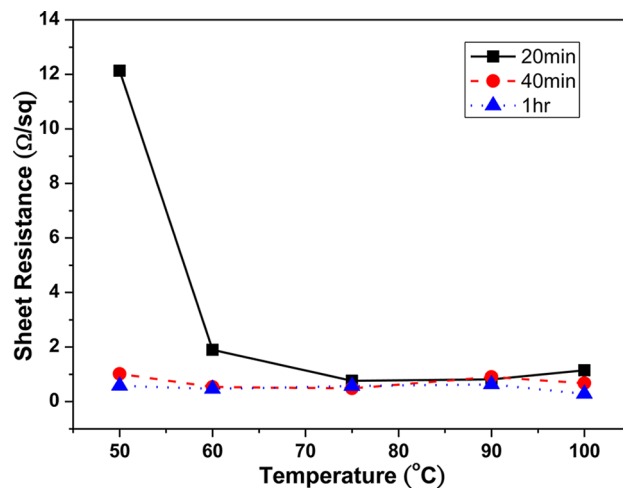
Effects of Post-treatment Temperatures on the Electrical Resistivity. The appropriate temperature window for the serial reaction can be determined from thermogravimetric analysis (TGA). Figure 3 shows the thermal analysis data for the ink (1:1 Ag$^+$/DEA ratio) heated in air at a rate of 10 °C/min. A broad valley is presented at low temperatures in the differential thermal analysis (DTA), indicating that the solvents keep evaporating below 120 °C. Because of the low
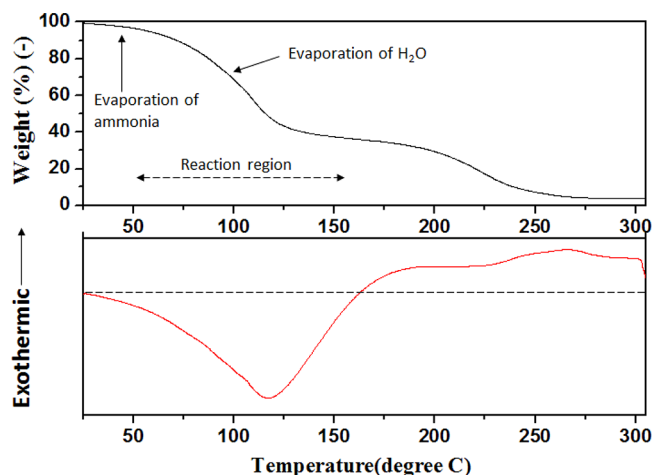
boiling point of ammonia (35 °C), a gradual mass loss between 20 and 60 °C is observed because of the volatility of ammonia. The mass curve falls rapidly above 60 °C and reaches a plateau of ~30% at 120 °C, indicating the total evaporation of the solvents except DEA, which has a high boiling point of 270 °C. Because the serial reactions in eqs 1 and 2 require the existence of both water and silver ammonia, the reaction or heating temperature is chosen to be within 50−100 °C in the following sections to avoid incomplete reaction due to solvent evaporation.

To further investigate the effects of the heating process on the electrical resistivity, the sheet resistance of drop-cast films was first measured. An ink droplet of 30 μL was placed on a PET sheet and heated on a hot plate at temperatures between 55 and 100 °C for 20−60 min. Silver thin films were synthesized on the droplet spots quickly after the thermal treatment. Because of the excessive DEA amount and its high boiling temperature, an oily liquid thin film composed of concentrated DEA was formed above the silver film. After rinsing with water to remove the residue components, drop-cast silver films were created. Figure 4 shows the relationship between the sheet resistance and heating temperatures. For


Figure 4. Variation in the sheet resistance of drop-cast films with the baking temperature.

post-treatment temperatures lower than 75 °C, the film resistance reduces as the thermal heating time increases, indicating that the silver recovery rate is fairly slow and leads to thinner silver nanoparticle deposition. On the other hand, when a temperature higher than 75 °C is used, DEA decomposition can be fast enough for silver recovery and the silver ammonium ions are totally consumed within 20 min. Thus, a heating temperature higher than 75 °C might be necessary to shorten the postprocess to within 20 min.

Printing or Writing Patterns. Inkjet-printed tracks on PET substrates are also used to investigate the effects of post-treatment temperatures on the boundary definitions of printed micropatterns. To reduce the process time, a 20 min heating period was used here. When a heating temperature of 55 °C was used, the boundary of the printed silver tracks was straight; however, because of the slow reaction rate, as shown previously in Figure 4, the electrical resistance of the synthesized silver films was fairly large. To increase the silver deposition rate, one can increase the thermal heating temperature. However, if the heating temperature is higher than 90 °C, the solvent evaporation can lead to bubbling in the thermal post-treatment and leaves conductive silver thin films with shattered boundaries (Figure 5). The optimum temperature was found
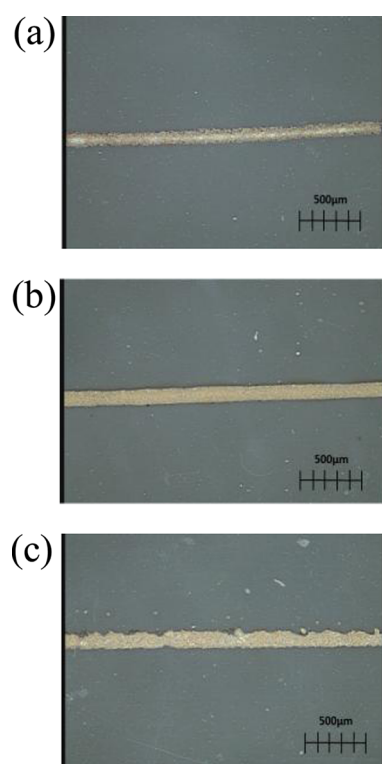
Figure 5. Images of inkjet-printed lines after thermal post-treatment at (a) 55, (b) 75, and (c) 100 °C for 20 min.

to be 75 °C; the printed tracks have well-defined boundaries with low electrical resistivity. The samples have an average film thickness of 150 nm, and the calculated electrical resistivity is 6 $\mu\Omega$-cm, or equivalently 26% conductivity of bulk silver (1.6 $\mu\Omega$-cm). The high conductivity of the printed tracks indicates that the silver conversion from this decomposition/reduction approach is high enough to convert silver ions into thin films with compact nanoparticle packing despite the low silver content in the ink (~3 wt %). Besides inkjet printing, this ink

can also be applied in any direct-writing or printing techniques. As demonstrated in Figure 6a, one can fill the silver ink into a
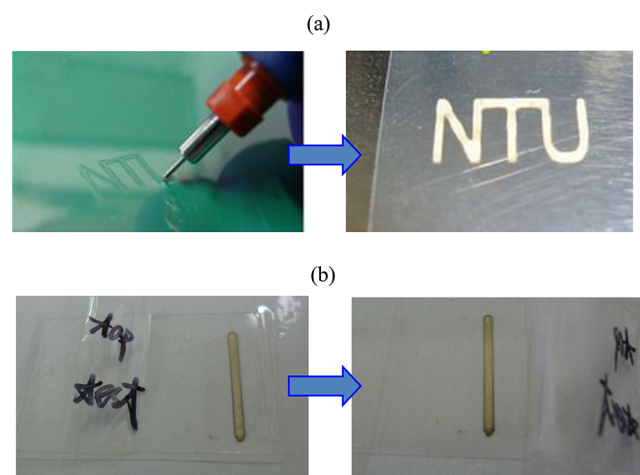

Figure 6. (a) Images for pen-written silver thin films. (b) Tape test for a pen-written silver thin film. For visual effects, a line of 2 mm in width was used.

regular plotter pen, draw patterns on PET surfaces, and transform the patterns into conductive silver thin films with a simple thermal post-treatment. The pen-written films, which were produced by a thick layer of ink liquids, can be as thick as micrometers and exhibit white color after post-treatment. Moreover, the silver films attach to the PET sheets fairly well and cannot be removed except with harsh scratches. As shown in Figure 6b, a simple tape test was performed to examine the adhesion of synthesized silver films. The silver films stayed on the plastic surfaces completely after removal of the attached tape (Scotch Cat. 600 tape, 3M), indicating great adhesion between the printed silver films and PET surfaces.

Microstructure Characterization. The microstructures of printed silver thin films are examined by scanning electron microscopy (SEM). Figure 7a shows the SEM micrographs of printed silver tracks on PET sheets, after rinsing with water. The printed silver tracks consist of a uniform thin film packed by silver nanoparticles of 80−100 nm diameter. X-ray diffraction (XRD) is also used to probe the crystalline structures in the printed samples. XRD patterns of printed silver films show sharp distinct peaks (Figure 7b) at 2θ values of about 38, 44, 64, and 77, which are all in good agreement with the characteristic values for metallic silver crystalline.[13,20] The reflection peaks are indexed as the (111), (200), (220), and (311) plane Bragg's reflections of the face-centered-cubic (fcc) structure of silver, indicating that silver is well crystallized; i.e., the synthesized silver thin films are composed of pure silver. Moreover, the ratio of the intensity between the (111) and (200) peaks has a relatively high value of 3.2 (the theoretical ratio is 2.5), indicating the enrichment of fcc (111) crystalline planes in the silver films.[20]

■ CONCLUSIONS

A simple silver ink with self-reduction nature is developed to synthesize silver thin films on PET sheets. DEA, a self-decomposing compound at mild elevated temperatures, was mixed with a silver ammonia solution to form a clear and stable solution. After heating at temperatures above 50 °C, DEA decomposes and generates formaldehyde, which reacts
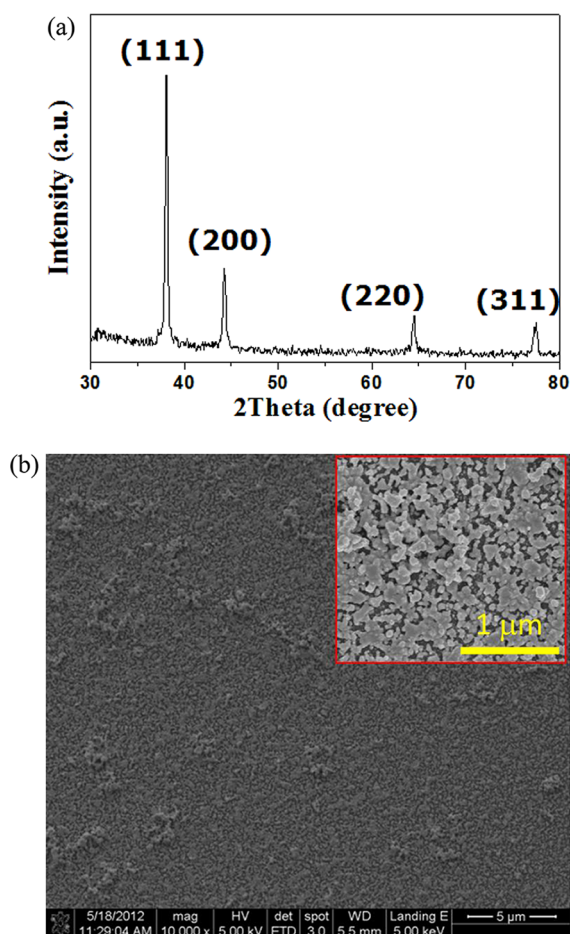
Figure 7. (a) XRD patterns and (b) SEM images of inkjet-printed silver tracks. The tracks were obtained with thermal post-treatment at 75 °C for 20 min.

spontaneously with silver ammonia ions to form silver nanoparticle stacking on plastic surfaces. The prepared ink was found to be stable for inkjet printing within 24 h at room temperature. From TGA, evaporation of the solvents was found to be predominant at temperatures higher than 100 °C, and thus the heating temperature for the post-treatment was chosen to be between 50 and 100 °C. The electrical conductivity of inkjet-printed silver tracks was found to be best with a thermal post-treatment at 75 °C for 20 min. The resistivity of the printed silver material as calculated from the resistance and cross-sectional area of the printed tracks is 6 $\mu\Omega$-cm, or ~4 times that of pure silver. SEM showed that printed silver films were formed by a stack of fused silver nanoparticles of 80−100 nm diameter. XRD patterns identify that the printed silver films are comprised of fcc nanocrystalline phases. The ink can also be used to create conductive silver patterns with pen-writing technology, and the resulting silver thin films adhered fairly well on PET sheets. This silver ink could be useful for the printing of conductive tracks in various applications, such as embedded printed circuit boards, micro-electromechanical systems, and RFID tags.

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■ REFERENCES

(1) Yoon, B.; Ham, D. Y.; Yarimaga, O.; An, H.; Lee, C. W.; Kim, J. M. *Adv. Mater.* **2011**, *23*, 5492−5479.
(2) Costa, C.; Pinheiro, C.; Henriques, I.; Laia, C. A. T. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1330−1340.
(3) Maattanen, A.; Ihalainen, P.; Pulkkinen, P.; Wang, S. X.; Tenhu, H.; Peltonen, J. *ACS Appl. Mater. Interfaces* **2012**, *4*, 955−964.
(4) Eom, S. H.; Senthilarasu, S.; Uthirakumar, P.; Yoon, S. C.; Lim, J.; Lee, C.; Lim, H. S.; Lee, J.; Lee, S. H. *Org. Electron.* **2009**, *10*, 536−542.
(5) Perelaer, J.; Smith, P. J.; Mager, D.; Soltman, D.; Volkman, S. K.; Subramanian, V.; Korvink, J. G.; Schubert, U. S. *J. Mater. Chem.* **2010**, *20*, 8446−8453.
(6) Subramanian, V.; Frechet, J. M. J.; Chang, P. C.; Huang, D. C.; Lee, J. B.; Molesa, S. E.; Murphy, A. R.; Redinger, D. R. *Proc. IEEE* **2005**, *93*, 1330−1338.
(7) Perelaer, J.; Klokkenburg, M.; Hendriks, C. E.; Schubert, U. S. *Adv. Mater.* **2009**, *21*, 4830−4834.
(8) Tekin, E.; Smith, P. J.; Schubert, U. S. *Soft Matter* **2008**, *4*, 703−713.
(9) Allen, M. L.; Aronniemi, M.; Mattila, T.; Alastalo, A.; Ojanpera, K.; Suhonen, M.; Seppa, H. *Nanotechnology* **2008**, *19*, 175201.
(10) Lee, K. J.; Jun, B. H.; Kim, T. H.; Joung, J. *Nanotechnology* **2006**, *17*, 2424−2428.
(11) Perelaer, J.; Hendriks, C. E.; de Laat, A. W. M.; Schubert, U. S. *Nanotechnology* **2009**, *20*, 165303.
(12) Reinhold, I.; Hendriks, C. E.; Eckardt, R.; Kranenburg, J. M.; Perelaer, J.; Baumann, R. R.; Schubert, U. S. *J. Mater. Chem.* **2009**, *19*, 3384−3388.
(13) Kao, Z. K.; Hung, Y. H.; Liao, Y. C. *J. Mater. Chem.* **2011**, *21*, 18799−18803.
(14) Valeton, J. J. P.; Hermans, K.; Bastiaansen, C. W. M.; Broer, D. J.; Perelaer, J.; Schubert, U. S.; Crawford, G. P.; Smith, P. J. *J. Mater. Chem.* **2010**, *20*, 543−546.
(15) Jahn, S. F.; Blaudeck, T.; Baumann, R. R.; Jakob, A.; Ecorchard, P.; Ruffer, T.; Lang, H.; Schmidt, P. *Chem. Mater.* **2010**, *22*, 3067−3071.
(16) Wu, J. T.; Hsu, S. L. C.; Tsai, M. H.; Hwang, W. S. *J. Phys. Chem. C* **2011**, *115*, 10940−10945.
(17) Walker, S. B.; Lewis, J. A. *J. Am. Chem. Soc.* **2012**, *134*, 1419−1421.
(18) Krutyakov, Y. A.; Kudrinskiy, A. A.; Olenin, A. Y.; Lisichkin, G. V. *Russ. Chem. Rev.* **2008**, *77*, 242−269.
(19) Kao, Z.-K.; Chen, S.-P.; Lin, J.-L.; Liao, Y.-C. *J. Taiwan Inst. Chem. Eng.* **2012**, *43*, 965−970.
(20) Sun, Y. G.; Yin, Y. D.; Mayers, B. T.; Herricks, T.; Xia, Y. N. *Chem. Mater.* **2002**, *14*, 4736−4745.
(21) Wu, Y.; Li, Y.; Ong, B. S. *J. Am. Chem. Soc.* **2007**, *129*, 1862−1863.
(22) Li, Y.; Wu, Y.; Ong, B. S. *J. Am. Chem. Soc.* **2005**, *127*, 3266−3267.
(23) Puttaswamy, M.; Vaz, N.; Gowda, N. M. M. *Int. J. Chem. Kinet.* **2001**, *33*, 480−490.
(24) Mahltig, B.; Gutmann, E.; Meyer, D. C.; Reibold, M.; Bund, A.; Bottcher, H. *J. Sol−Gel Sci. Technol.* **2009**, *49*, 202−208.
(25) Meltsner, M.; Wohlberg, C.; Kleiner, M. J. *J. Am. Chem. Soc.* **1935**, *57*, 2554−2554.
(26) Zhou, J.; Zhao, G. L.; Ren, X. X.; Song, B.; Han, G. R. *J. Sol−Gel Sci. Technol.* **2011**, *58*, 148−155.