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Comparison of thermal decomposition and chemical reduction of particle-free silver ink for inkjet printing

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ABSTRACT

Two current major methods (thermal decomposition of silver organic salts and chemical reduction of silver salts) to formulate a particle-free silver ink are compared. X-ray diffraction (XRD) and scanning electronics microscopy (SEM) are used to investigate the printed silver patterns from conductive inks made from those two methods. Both processes are shown to make silver with high purity from XRD results. SEM images indicate that chemical reduction can make denser silver film than thermal decomposition. Thermogravimetric analysis and Differential thermal analysis indicates that the silver film is formed at very low temperature compared with thermal decomposition. This phenomenon may be caused by volume shrinkage of silver precursor decomposition after thermal sintering. The resistivity of printed silver patterns made by chemical reduction is also lower than the silver patterns made by thermal decomposition because of less porosity. Also, our results show that a polymer additive can render the silver film more uniform and easier to be sintered.

1. Introduction

Increasing attention has been devoted to printable circuit boards, sensors and smart ID cards by using conductive/functional inks [1–6]. The principle of printable electronics is to deposit conductive/functional ink on flexible substrate by printing technologies (*e.g.* inkjet or screen printing) [7,8]. The most used substrate is Kapton (polyimide) because of its stable physical and chemical properties especially at relatively high temperature [9–11]. The printed patterns are then treated with sintering processes to obtain required electrical and mechanical properties. Various sintering processes like thermal, microwave, plasma and photonic sintering [12–15] have been studied.

The key step of making printable devices is ink formulation. Commercially available conductive inks are usually metal nanoparticle (copper [16,17], platinum [18], nickel [19], silver [20–22]) dispersed in organic/aqueous solvents. Among those materials, silver has high electrical conductivity, relatively low melting point and excellent chemical stability while sintered in air; those advantages make silver nanoparticle ink the most widely used for printing conductive devices. However, nanoparticle-based ink still requires high sintering temperature to join particles. Also, nanoparticle-based inks have limited printing resolution and reliability due to nozzle clogging issue during printing. Alternatively, particle-free silver inks have been developed to avoid nozzle clogging and achieve high resolution printing. Generally, silver salt complex solution is used as a particle free ink, after printing, drying and sintering, the silver complex is transformed into highly conductive silver thin film; the thermal treating temperature for particle-free ink is usually lower than the temperature required for nanoparticle-based ink. In particle-free silver ink, silver is produced by different chemical processes: (a) thermal decomposition of silver precursor like silver citrate [23,24], Ag(acetate)(ethanolamine)$_2$ [25], silver oxalate [13] and other synthesized organometallic silver [26]; (b) reducing of silver complex [27–32] by external reductants. The former process usually occurs after solvent evaporation, and then the silver complex degrades to silver by disproportionation reaction during sintering. In contrast, the latter one occurs before solvent evaporation. Both methods can produce high quality silver conductive film. Unfortunately, no report compares the difference between those two chemical processes.

In this article, different silver films synthesized by thermal decomposition and chemical reduction are compared. In order to eliminate the production diversity caused by silver sources, silver citrate is used as silver precursor for both ink formulations, which is able to

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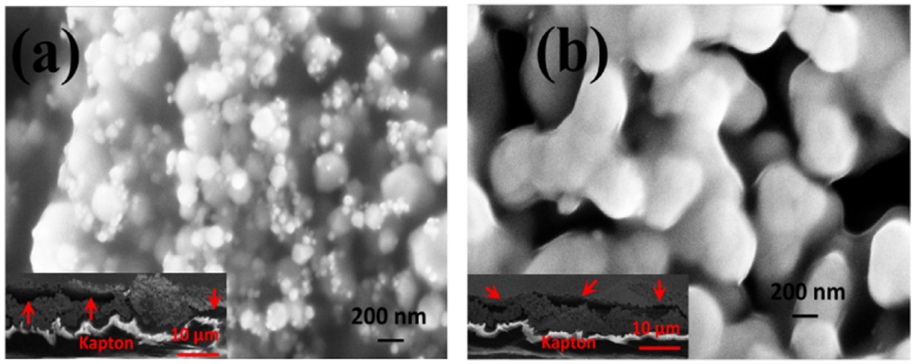
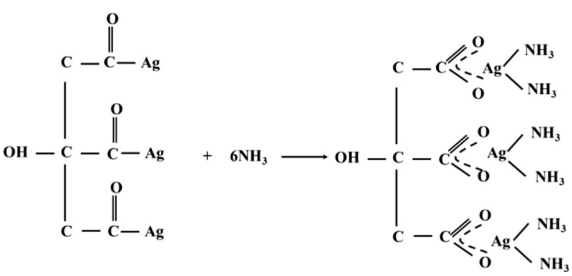


Fig. 1. SEM images of silver samples made by thermal decomposition: (a) without NaCMC and (b) without NaCMC. The insets are the cross section of the silver on Kapton. All the samples are sintered at 225 °C for 30 min.

decompose into silver and easily dissolved in water with the present of ammonia functional as complex agent shown in the follow equation [26,28]:



(1)

Dimethylformamide (DMF) is used as a mild reductant to reduce silver complex in aqueous solution by silver mirror reaction. Unlike normal Tollens reagents, no silver oxide intermediate produced during silver citrate dissolution which might react with ammonia to produce explosive silver azide [33]. Some research also report that a stable, non-explosive silver organic solution can be obtained by avoiding using Tollens reagents [24,32]. On the other hand, silver citrate contains almost the same amount of silver element as silver nitrate in Tollens reagents (silver citrate: 63 wt%, silver nitrate: 64 wt%). The existence of hydrophilic —OH groups on silver citrate is capable to increase the solubility of the silver complex by forming hydrogen bonds with water [25]. The influence of a sodium carboxymethyl cellulose (NaCMC) polymer additive is also investigated in this research. We analyze and demonstrate a formulation of particle-free silver ink which has excellent stability, printability and capability to produce silver with high electrical conductivity.

2. Experimental procedure

2.1. Materials

All of the chemical reagents used in the experiments are purchased from commercial sources with analytical purity and used without further purification. Silver citrate, ammonia, propanol alcohol, sodium carboxymethyl cellulose (NaCMC) and dimethylformamide (DMF) are purchased from Sigma Aldrich, USA. The formulated silver inks are deposited on Kapton film from Dupont Company, USA.

2.2. Synthesis of particle free silver ink

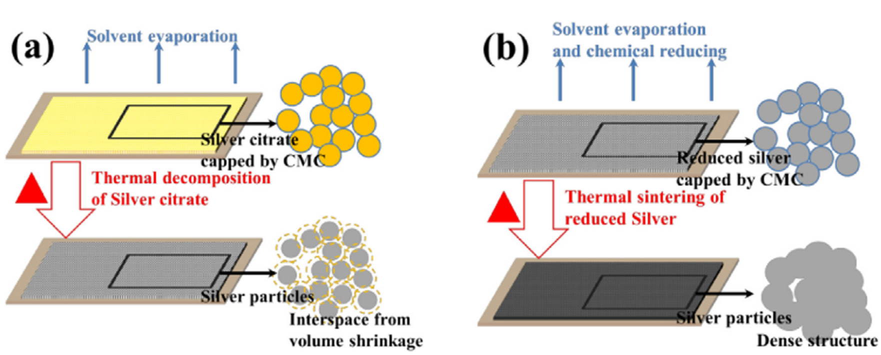
2.2.1. Thermal decomposable silver ink without NaCMC

The ink solvent is made by mixing 1 g Deionized (DI) water and 1 g ammonia. After adding 1 g silver citrate to the solvent, the mixture is ultrasonicated for 15 min to produce silver ammonia complex solution. The final viscosity is adjusted by adding propanol alcohol to meet the requirement of printer (around 10 cp). The solution is pressed

through a 0.5 μm syringe filter to eliminate large particles and other chemical remains. A clean and transparent particle free solution is obtained.

2.2.2. Thermal decomposable silver ink with NaCMC

0.15 wt% NaCMC solution is prepared by dissolving NaCMC in DI water at 50 °C and magnetic stirred for 30 min. 1 g NaCMC solution, 1 g ammonia and 1 g silver citrate is mixed, the mixture is ultrasonicated for 15 min to produce silver ammonia complex solution. The viscosity of silver ink is adjusted by adding propanol alcohol. The final NaCMC concentration is 0.05 wt%. NaCMC is used as polymer capping agent and film former [34].



Scheme 1. Of silver film made by (a) thermal decomposition and (b) chemical reduction.