

Preparation and Characterization of Organic Silver Precursors for Conductive Ink

Wendong Yang, Changhai Wang, Valeria Arrighi

Abstract—Low ink sintering temperature is desired for flexible electronics, as it would widen the application of the ink on temperature-sensitive substrates where the selection of silver precursor is very critical. In this paper, four types of organic silver precursors, silver carbonate, silver oxalate, silver tartrate and silver itaconate, were synthesized using an ion exchange method, firstly. Various characterization methods were employed to investigate their physical phase, chemical composition, morphologies and thermal decomposition behavior. It was found that silver oxalate had the ideal thermal property and showed the lowest decomposition temperature. An ink was then formulated by complexing the as-prepared silver oxalate with ethylenediamine in organic solvents. Results show that a favorable conductive film with a uniform surface structure consisting of silver nanoparticles and few voids could be produced from the ink at a sintering temperature of 150 °C.

Keywords—Conductive ink, electrical property, film, organic silver.

I. INTRODUCTION

IN recent years, organic silver inks tailored for flexible electronics have received increasing attention because of their convenience in preparation, excellent stability and low cost [1]-[5]. These inks can be utilized in a variety of applications such as circuit boards or RFID antenna. Generally, such inks consist of organic silver salts or silver organic complexes and volatile organic solvents which provide the essential rheological properties for various patterning technologies. As silver is usually in an ionic form within the ink, there is no aggregation issue during preparation, storage and patterning process, which is a key advantage. After patterning onto substrates, the organic solvent of inks is evaporated leaving the silver salt as a deposit, which can be subsequently decomposed or reduced by thermal treatment to form conductive patterns.

Favorable conductivity at temperatures below 150°C is desirable as it would widen the application of silver organic inks on substrates that are temperature-sensitive such as polymers. Therefore, the design of ink formulation becomes important, where the selection of silver precursors, complexing agents and volatile organic solvents is very critical because

these determine the final thermal and electrical properties of the ink.

To date, several kinds of organic silver salt precursors were selected to formulate organic silver inks. Silver neodecanoate was firstly used as a precursor to form organic silver inks, which starts to decompose to silver at 170°C, and full decomposition achieved at 250°C [6], [7]. Then, Jahn et al. [8] reported an organic silver ink based on 2-[2-(2-methoxyethoxy)ethoxy] acetate silver. The ink was used for piezo ink-jet printing on PET substrates resulting in conductive layers with conductivity of 18% of the bulk silver. In 2012, Nie et al. [4] reported an organic silver ink synthesized using silver citrate with 1, 2-diaminopropane for printing on PET substrates. Walker et al. [1] developed a low-viscosity and highly conductive silver ink based on a modified Tollens' process using silver acetate, suited for direct-writing, ink-jet printing and airbrush-spraying, which is attractive for plastic electronics applications. Chang et al. [2] prepared a novel ink of silver amide complex dispersed in glycol-water mixture. Silver ions in the solution can be reduced to metallic silver by glycol, following the typical polyol process. Yu et al. [9] synthesized a transparent and high-efficiency organic silver ink with silver acetate as silver carrier, ethanolamine as additive and dimethylformamide or formic acid as the reduction agent. Recently, Dong et al. [10] prepared organic silver inks using silver tartrate and various amines in ethyl alcohol. Black et al. [11] synthesized an organic silver ink with silver hexafluoroacetylacetonate cyclooctadiene as a precursor. Overall, each precursor has its advantages and disadvantages. For instance, silver neodecanoate, silver acetate silver carbonate and silver tartrate have a relatively high decomposition temperature (>170°C) and can decompose in the presence of light. 2-[2-(2-methoxyethoxy)ethoxy] acetate silver are stable but the synthesis is relatively complex. Therefore, it is necessary to develop new organic silver precursors for the conductive ink towards the flexible electronics.

In this paper, four types of organic silver precursor were prepared. Their physical phase, chemical composition and thermal behavior of them were investigated in detail by using various characterization methods. Then, the synthesized silver precursor possessing good property was chosen to formulate a conductive ink with solvents and amine complexing agent. The results show that silver films derived from silver oxalate ink had favorable conductivity after sintering at 150°C, which enabled the ink to be applied on temperature sensitive flexible substrates.

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II. EXPERIMENTAL SECTION

A. Materials

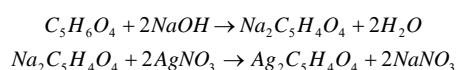
Silver nitrate (AgNO_3), itaconic acid ($\text{C}_5\text{H}_6\text{O}_4$), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), Sodium tartrate dibasic dihydrate ($\text{C}_4\text{H}_4\text{Na}_2\text{O}_6$), ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$), ethylene glycol ($\text{C}_2\text{O}_2\text{H}_6$) and ethanol ($\text{C}_2\text{H}_6\text{O}$) were obtained from Sigma-Aldrich and were used as received without further purification. The substrate, polyimide film (PI), was obtained from DuPont (127 μm in thickness). Before application, 15 mm \times 15 mm PI samples were cleaned using deionized water and ethanol to remove particles and organic contamination.

B. Synthesis of Organic Silver Precursors

In this work, four kinds of silver carboxylate possessing ideal structure characteristics were prepared through an ion exchange method. Among them, silver itaconate and silver oxalate were synthesized by using their corresponding organic acid sodium salt and silver nitrate, while silver carbonate was produced through the reaction of sodium carbonate and silver nitrate directly. Detailed processes and related chemical reactions are as follows:

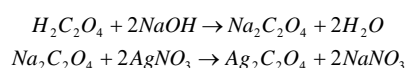
1) Silver Itaconate

Itaconic acid (0.65 g) and sodium hydroxide (0.4 g) were dissolved in 20 ml of deionized water respectively, the solutions mixed and stirred for 30 min at room temperature. Then, 10 ml of silver nitrate solution (1.7g AgNO_3) was added to the above mixture. After an hour of stirring in the absence of light, the product with white color was collected by vacuum filtration and washed with water for three times and ethanol twice, dried at 40°C for 8 h in an oven and stored both away from light. The obtained silver itaconate is about 1.491 g with a yield of 86.74%.



2) Silver Oxalate

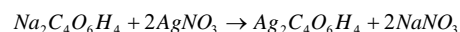
Oxalic acid (0.45 g) and sodium hydroxide (0.4 g) were dissolved in 10 ml of deionized water respectively, the solutions mixed and stirred for 30 min at room temperature. Then, 10 ml of silver nitrate solution (1.7g AgNO_3) was added to the above mixture. After an hour of stirring in the absence of light, the white product, silver oxalate, was collected by vacuum filtration and washed with water for three times and ethanol twice, dried at 40°C for 8 h in an oven and stored both away from light. The obtained silver oxalate was about 1.440 g with a yield of 94.81%.



3) Silver Tartrate

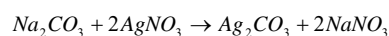
Sodium tartrate dibasic dihydrate (1.15 g) was dissolved in 10 ml of deionized water. Then, 1 ml of silver nitrate solution (1.7g AgNO_3) was added to the above solution. After an hour of

stirring in the absence of light, the white product was collected by vacuum filtration and washed with water for two times and ethanol once, dried at 40°C for 8 h in an oven and stored both away from light. The obtained silver tartrate was about 1.438 g with a yield of 79.05%.



4) Silver Carbonate

Sodium carbonate (0.53 g) was dissolved in 10 ml of deionized water. Then, 10 ml of silver nitrate solution (1.7 g AgNO_3) was added to the above solution. After an hour of stirring in the absence of light, the yellow product was collected by vacuum filtration and washed with water for two times and ethanol once, dried at 40°C for 8 h in an oven and stored both away from light. The obtained silver oxalate powder was about 1.037 g with a yield of 75.69%.



C. Ink Preparation, Deposition and Sintering

For ink preparation, 0.152 g of silver oxalate was dispersed in 0.75 ml of a mixed solvent containing ethanol (0.375 ml) and ethylene glycol (0.375 ml). After stirring for 5 minutes, ethylenediamine (0.134 ml) was added. The mixture was stirred for 60 min to form the ink that was a homogeneous transparent solution. The silver content in the ink was about 10 wt%. The as-prepared ink was then deposited on the PI films by a drop-coating method, and sintered at 150°C for up to 60 min. The film thickness was controlled by the volume of ink solution deposited onto the PI film.

D. Characterization

The crystallite phases of the obtained silver carboxylate powders were identified by X-ray diffraction (XRD) using Cu K α radiation ($\lambda = 0.15418$ nm). The thermal decomposition behaviors were investigated by differential scanning calorimetry (DSC) and thermogravimetry (TG) at a heating rate of 10°C min⁻¹ from room temperature to 250°C under a nitrogen atmosphere. A fourier transform infrared (FT-IR) spectrometer (Thermo Scientific Nicolet iS5) were used to analyze the chemical structures of the prepared powders and ink. A surface energy disperse spectrometer (EDX, Oxford X-maxN 150) was used to analyze the chemical composition. The surface morphologies of the silver films after sintering were observed using a FEI Quanta 3D Scanning Electron Microscope (SEM). The resistivity of the silver film was calculated from the sheet resistance together with the thickness of the film. The sheet resistivity of the film was measured using a 4-point probe method (Jandel Engineering, UK). The thickness of the films was obtained using a Dektak surface profilometer.

III. RESULTS AND DISCUSSION

A. Structure and Phase Confirmation of Silver Carboxylates

As a component of the ink, selection of silver precursors was very important because it determines the final thermal and

electrical properties of the ink. To some extent, silver aliphatic carboxylates unsaturated, branched and/or substituted with hydroxyl group, are mostly preferred because they are easy to be transformed into silver atom at low temperature via decarboxylation reaction. In this part, four types of silver carboxylate possessing the above structure characteristics were prepared and then were investigated to select the most ideal one for the subsequent ink preparation. FT-IR and XRD were first employed to confirm their structure and physical phase.

Fig. 1 shows the IR spectra of four as-prepared powders. For silver carboxylates, the peak in the range of 1650 cm^{-1} to 1550 cm^{-1} is attributed to the asymmetric stretching vibration of C=O in the carboxyl group (-COO-) while the peak in the range of 1440 cm^{-1} and 1350 cm^{-1} is from C=O symmetric stretching vibration. The peaks from 800 cm^{-1} to 200 cm^{-1} arise from vibrations of metal-O group and the band around 1073 cm^{-1} is from C-O stretch. The broad peak around 3200 cm^{-1} is assignable to the O-H stretching vibration. Take silver tartrate for an example, the broad feature around 3230 cm^{-1} is attributed to the stretching vibration of O-H. Two sharp peaks at 1610

cm^{-1} and 1560 cm^{-1} are attributed to the asymmetric stretch vibration of C=O whilst the peak at 1370 cm^{-1} is from the symmetric stretch vibration of C=O. These features indicate that silver tartrate has a structure of carboxylate substituted with hydroxyl. Similarly, the IR spectra of other three powders could also confirm that they are silver carboxylates.

Fig. 2 gives the XRD patterns of four as-prepared silver carboxylate powders. Of them, the data of silver carbonate, silver oxalate and silver tartrate are all in good agreement with that of their standard card, JCPDS No.26-0339, JCPDS No.022-1335 and JCPDS No.01-0441. No diffraction peaks from any other impurities were detected, indicating that the reaction was completed and these three kinds of powders were prepared successfully. For silver itaconate, we could not find its card in the XRD database but in combination with the results of DSC/TG shown later, this can be confirmed as there is only one exothermic peak on the DSC curve and 63.46 wt% of the remaining weight in TG curve is basically in line with the proportion of silver in the silver itaconate (62.75 wt%).

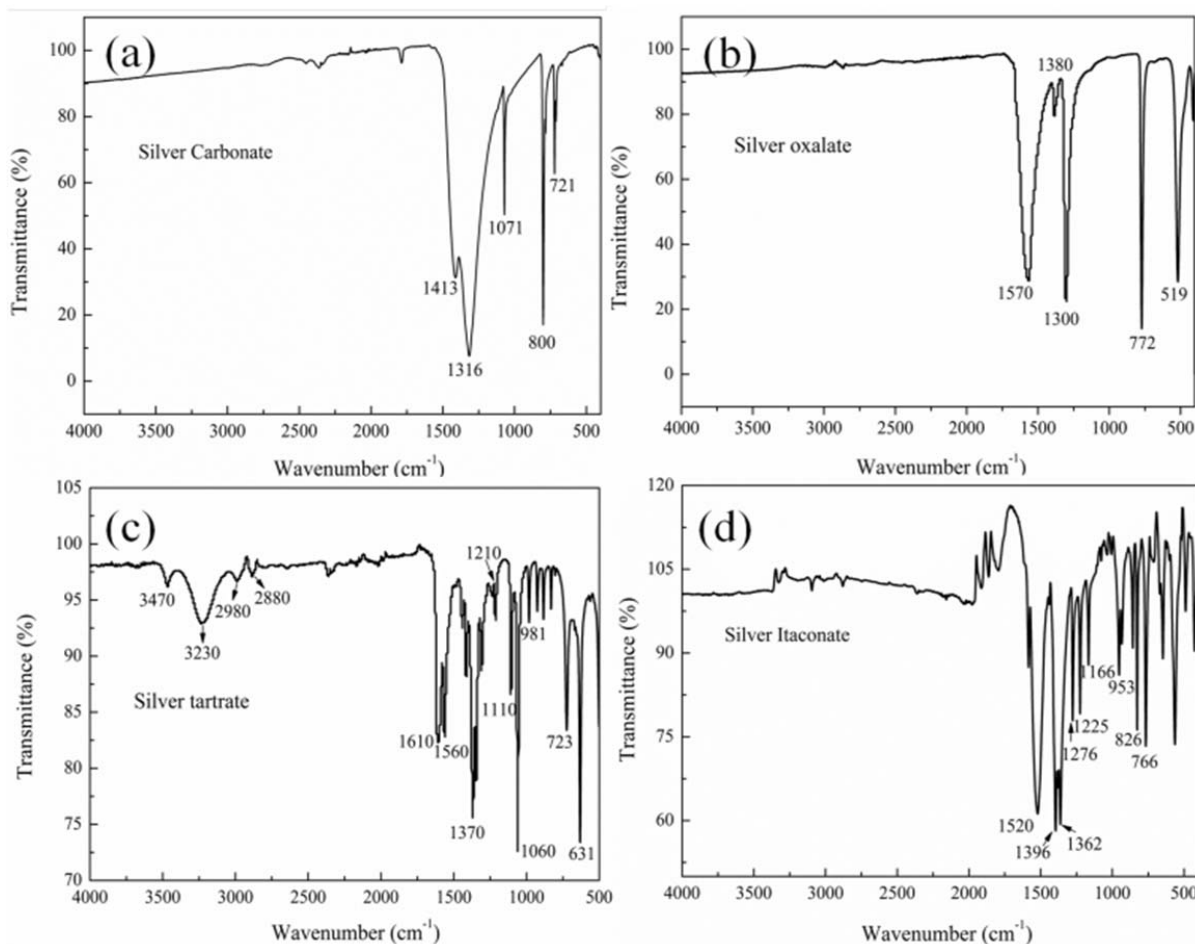


Fig. 1 FT-IR spectra of four as-prepared silver carboxylates

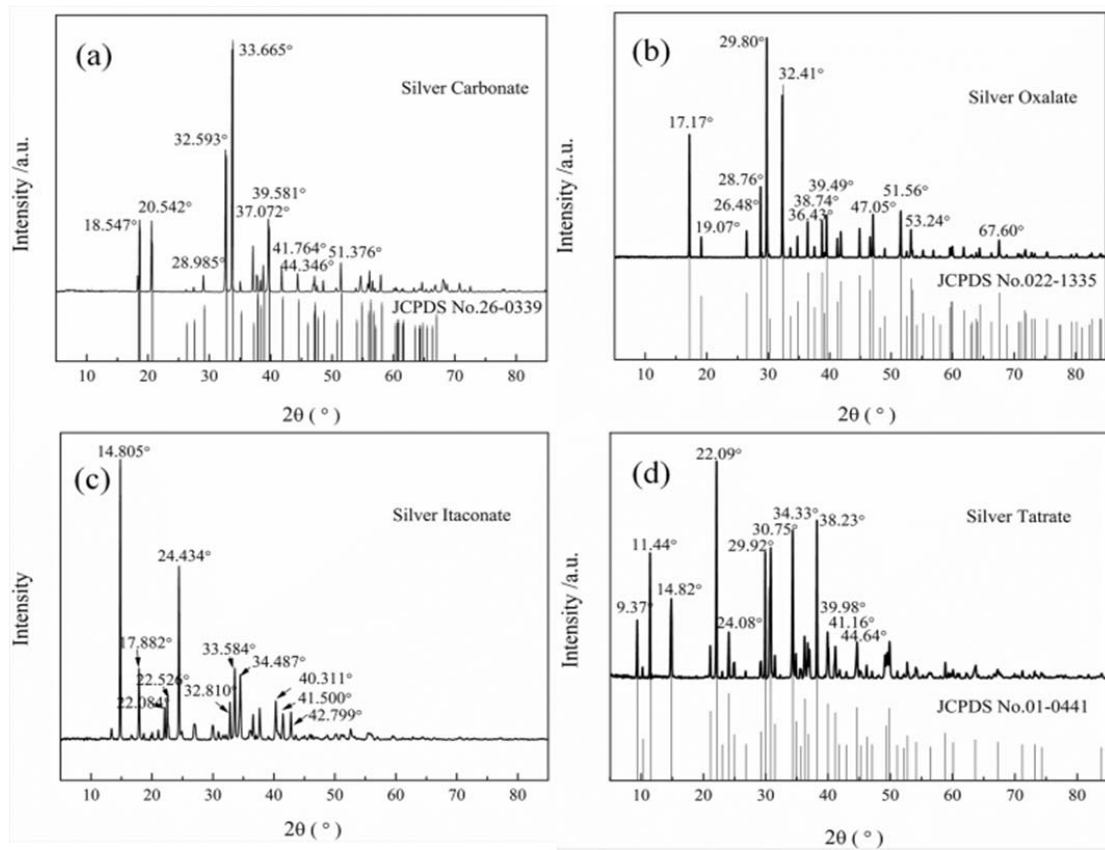


Fig. 2 XRD patterns of four as-prepared silver carboxylates

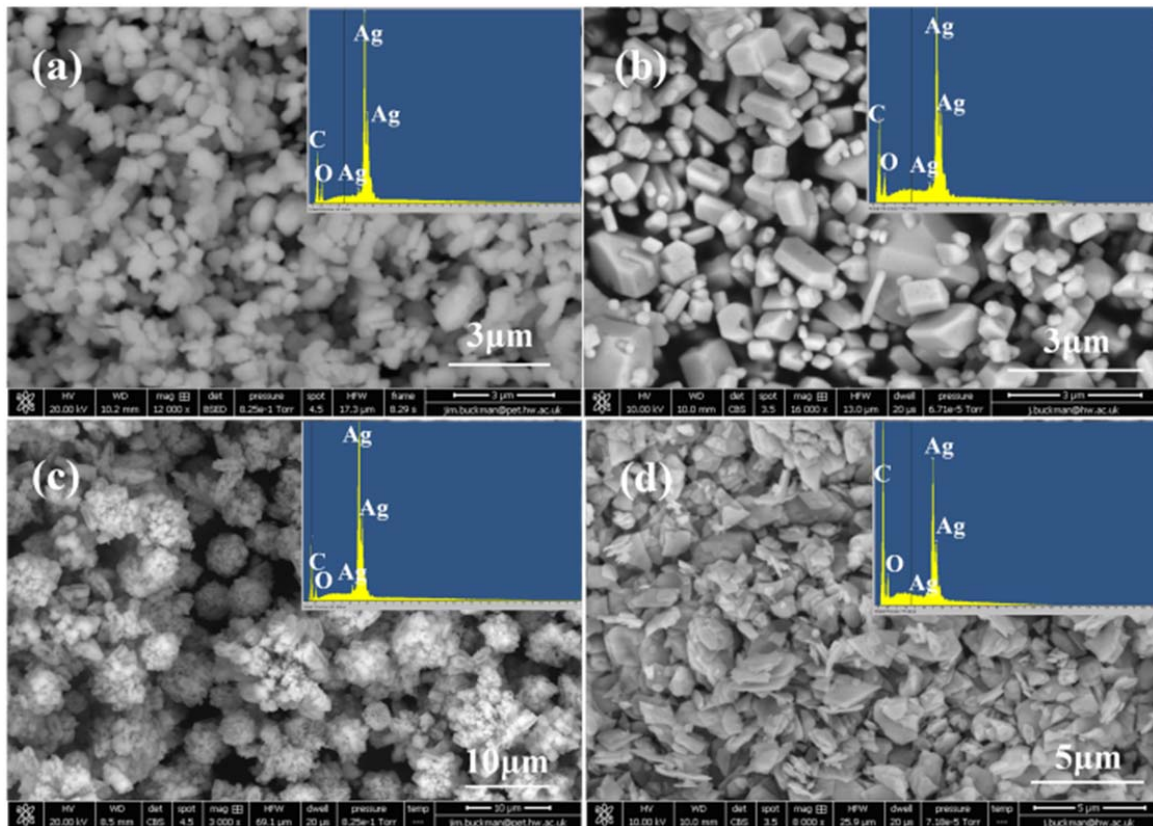


Fig. 3 SEM and EDX results of four as-prepared silver carboxylates

B. Chemical Composition and Surface Morphology

The morphology and chemical composition of the prepared powders was identified by SEM/EDX measurements as shown in Fig. 3.

Clearly, four powders have different morphologies. Silver carbonate showed oblique crystal structure with uniform particle size while the silver oxalate presented a hexagonal columnar morphology with two kinds of particle size, which is in agreement with the later DSC results where two peaks were observed. Silver itaconate showed a flowerlike morphology that is assembled by well-defined rectangular crystals and silver tartrate has a flake structure with a uniform particle size. The EDX measurements show that three elements (C, O, and Ag) exist in all powders, which well accords with the

original chemical composition of the compounds.

C. Thermal Behavior of Silver Carboxylates

Figs. 4 and 5 show the thermal behaviors of the four as-prepared powders. In the DSC curves, silver itaconate and silver tartrate have only one endothermic peak relating to the thermal decomposition of their powders, respectively. Silver carbonate has a complex thermal behavior compared to others. Silver oxalate gives the lowest decomposition temperature where the curve shows two endothermic peaks at 168°C and 190°C. As for the TG curves, it can be seen that the residual weight of each powder is basically in line with the proportion of silver in their complex, indicating that the decomposition product was almost metal silver.

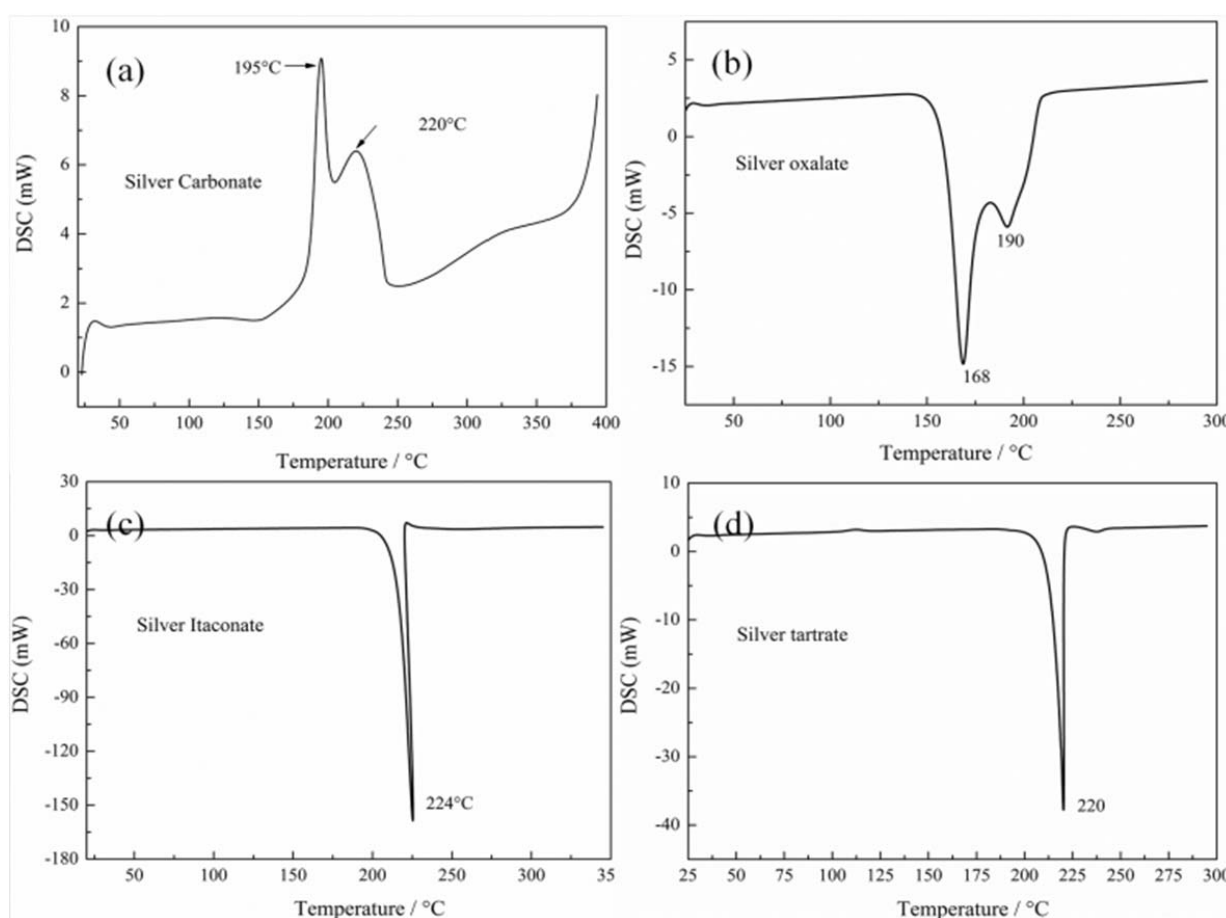


Fig. 4 DSC curves of four as-prepared silver carboxylates

Among them, the silver weight left by silver carbonate was the most after decomposition, but the temperature used to reach this data is too high for the ink application. Silver oxalate powder starts to lose weight at 150°C and reaches its maximal rate of weight loss at 200°C. The left weight is about 71.88 wt%, which is expected. As for the reason why they present different thermal behavior, there is not a unified view or theory but it should be related to their structures.

All results demonstrate that silver oxalate powder is an ideal precursor material for the ink preparation.

D. Ink Formulation and Thermal Behavior Investigation

For ink preparation, ethylenediamine was chosen as ligand to dissolve the silver oxalate in the alcohol solvent and further to decrease the ink sintering temperature. Ethanol was used as the solvent to adjust the surface tension and viscosity of the ink. Ethylene glycol was used as a co-solvent to suppress the undesirable coffee ring effect caused by ethanol in the film sintering process [11].

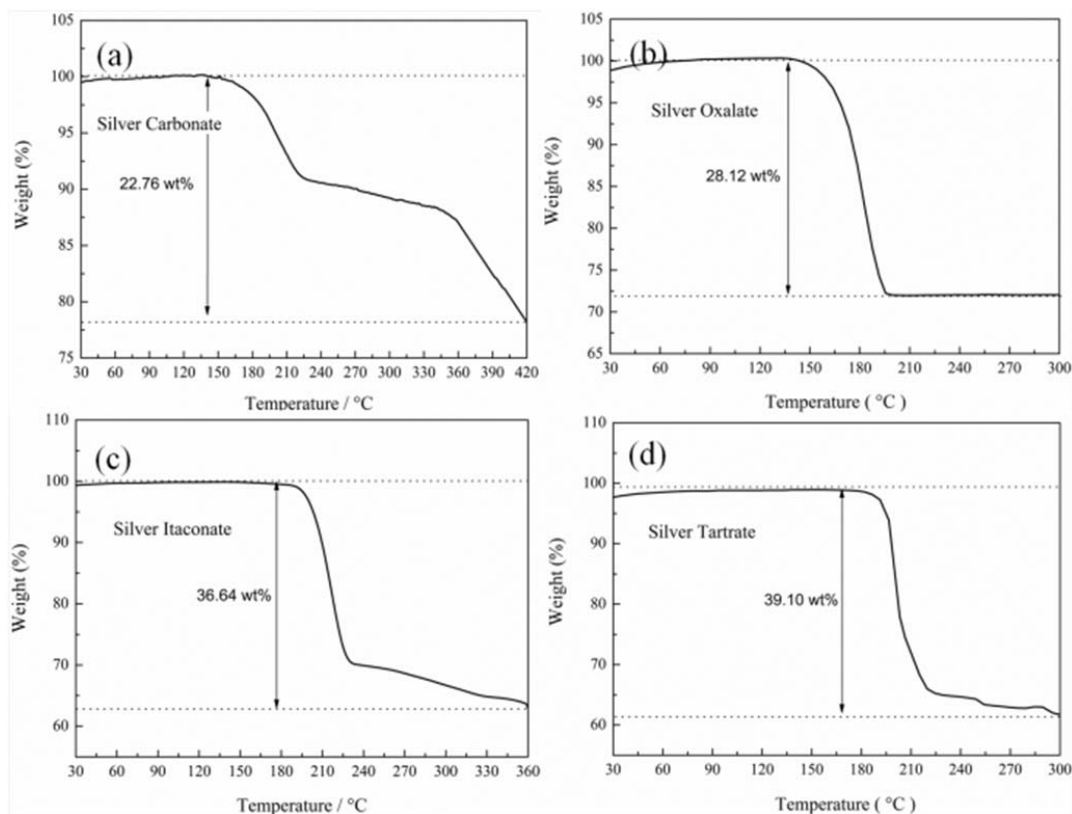


Fig. 5 TG curves of four as-prepared silver carboxylates

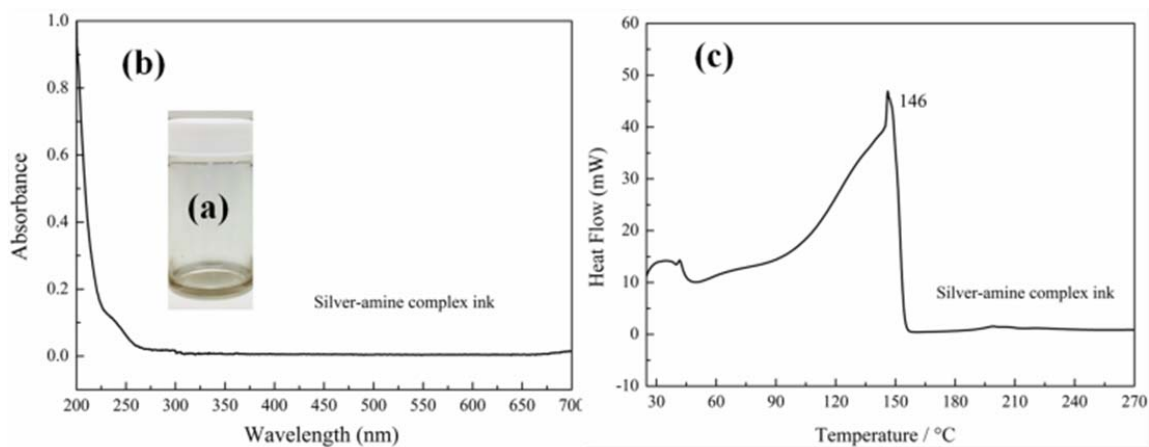
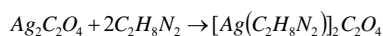


Fig. 6 As-prepared silver ink (a) and its UV-Vis absorption spectra (b) as well as DSC curve (c)

The as prepared ink was found to be transparent without particles or any impurities (Fig. 6 (a)), indicating the occurrence of following reaction. The lone pair electrons on the nitrogen of ethylenediamine coordinate with silver oxalate and form silver organic complex that is dissolvable in the alcohol solvent.



DSC analysis was carried out to investigate the thermal decomposition behavior of the as-prepared ink (Fig. 6). The endothermic peak below 60°C is due to evaporation of the free

amine and ethanol in the ink. The peak at 146°C is attributed to the decomposition of the silver complex and the evaporation or decomposition of ethylene glycol.

E. Microstructure of Silver Film

Silver films were produced by drop-coating of ink on the cleaned PI substrates. The sintering process was carried out on a hotplate in a chamber. Based on the DSC results of the ink, 150°C was used for the thermal sintering. Surface profilometry, XRD and SEM were employed to evaluate the produced silver films.

As the XRD spectrum shown in Fig. 7, it can be seen that

silver ions have transformed to silver nanocrystals within 60 minutes. Diffraction peaks observed at 2θ values of 38.2° , 44.4° , 64.5° , 77.5° and 81.6° well corresponds to the characteristic values for metallic silver.

Surface profile showed that the sintered film had an average

thickness of $1.3 \pm 0.3 \mu\text{m}$ with a relatively uniform surface structure where the silver nanoparticles accumulated at the centre and no 'coffee ring effect'. Along with the SEM result, it can be seen that a film with few voids was generated after sintering at 150°C for 60 min.

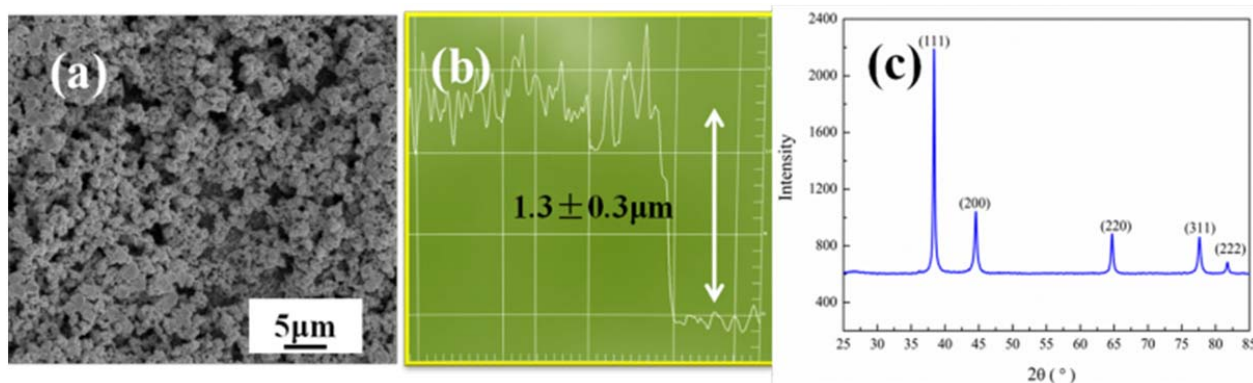


Fig. 7 SEM image (a), surface profile (b) and XRD pattern (c) of silver film sintered at 150°C for 60 minutes

F. Electrical Property

The resistivity of sintered silver film was calculated using the above thickness and the measured sheet resistance via (1), which was shown in Table I.

$$\rho = R_s \cdot t \quad (1)$$

where ρ is the resistivity, R_s is the sheet resistance of the Ag film, t is the average thickness of the film.

Clearly, the produced silver films have good conductivity after sintering at 150°C for 60 min ($<10^{-5} \Omega\cdot\text{cm}$). The resistivity decrease with increasing sintering time can be easily understood. In short time, the solvent evaporated partly and the formation of silver is not complete, so the film has high resistivity. On the contrary, for longer time, most solvent evaporated and more silver nanocrystals were formed and can contact with each other, thereby resulting in good film conductivity.

TABLE I

RESISTIVITY OF THE AG FILMS AS A FUNCTION OF HEATING TIME AT 150°C

Time (minutes)	Sheet Resistance ($\text{m}\Omega/\square$)	Resistivity ($\mu\Omega\cdot\text{cm}$)
10	431.59	56.10
30	355.51	46.21
60	305.82	39.75

It is useful to note that film resistivity of $10^{-5} \Omega\cdot\text{cm}$ achieved at 150°C has already met the requirements of most electronic applications, which would widen the application of the ink on various substrates including temperature sensitive substrates such as polyethylene terephthalate (PET).

IV. CONCLUSION

In summary, four types of organic silver precursors were synthesized via an ion exchange method firstly. FT-IR, XRD,

SEM/EDX and DSC-TG were employed to confirm their physical phase, chemical composition, morphologies and thermal decomposition temperature. Of them, silver oxalate showed the ideal property as it had a higher silver content and lowest decomposition temperature. An ink was then prepared using the complexing reaction between the as-prepared silver oxalate powder and ethylenediamine in a mixture of EG and EA solution, producing a favorable conductive film onto PI substrate at a sintering temperature of 150°C . The sintered film showed a homogeneous microstructure consisting of silver nanoparticles with few voids.

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