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Optimizing formulations of silver organic decomposition ink for producing highly-conductive features on flexible substrates: The case study of amines

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ABSTRACT

Highly conductive silver patterns that can be cured at low temperatures were achieved by proper selection of the kinds of amines in the formulation of metal organic decomposition (MOD) ink. The inks were synthesized via a complexing reaction between silver tartrate and various amines in ethyl alcohol solvent. Four monoamines and two diamines with increased carbon chain lengths were used. The kinds of amines affected the thermal decomposition temperature of silver ink as well as the sheet resistance and microstructure of the obtained silver films significantly. The film from 1,2-diaminopropane ink showed the lowest resistance and uniform surface morphology among all the inks developed. The microstructural evolution of the cured silver films was well correlated with the formulations of the inks. The underlying mechanism was discussed. The ink formulations were further elaborated by proper selection of Ag/NH_2 molar ratios. Highly conductive silver films with excellent flexible stability and great adhesion were achieved using optimized silver MOD inks.

1. Introduction

Printed electronics, which make uses of various printing methods to transfer inks of functional materials on substrates with fast speed and low cost, have attracted increased research interests recently [1–3]. Compared with the conventional photolithographical/etching processes, printed electronics offer a number of attractive virtues, such as reduced consumption of raw materials, environmental friendship, being adaptable to a number of simple manufacture processes and high productivity. One interesting research focus on printed electronics is the development of inks for patterning electrically conductive lines or features on flexible substrates, mainly for applications in a wide range of newly-emerged electronic devices, such as radio frequency identification tags [4], organic photovoltaics [5,6], organic light emitting diodes [7], thin film transistors [8], molecular diagnostic devices [9], etc.

Previously, printable conductive inks of a number of materials have been demonstrated, namely silver [10–22], copper [23,24], carbon [25], and conductive polymers [26], among them, silver has emerged as the material of choice since it is the best conductor that is also stable under normal operating conditions. Two types of silver-based inks have been frequently reported in the literatures: nanoparticle-based ink [10–13] and metal organic decomposition (MOD) ink [14–22]. While silver particle inks are widely adopted commercially, silver MOD ink has found increased research interests only recently. Compared with its solid-particle counterpart, MOD ink is a solution-based ink and provides a number of advantages. Firstly, unlike silver particle ink, which requires a high temperature to fuse the particles in sintering procedure, conductive patterns are formed directly by a thermal decomposition reaction of silver-containing compound for MOD inks. Consequently, desired high conductivity can be achieved at a much lower curing temperature than that of required for the sintering of silver nano-particles. This merit allows MOD inks to be applied in a wide range of emerging electronic devices, where flexible substrates are preferably adopted [15–22]. Secondly, MOD ink is essentially a solution. The problems such as nozzle clogging, which are frequently encountered in inkjet printing of particle inks, are totally avoided. In this regard, the latter merit allows features of extremely fine resolutions to be printed [16].

Previously, a number of research works on silver solution inks have been performed, mainly aimed at developing ink formulations leading to highly conductive patterns at lower temperatures [14–22]. Huang et al. [14] provided an ink similar to the true solution by complexing silver nitrate and NH_4OH, utilizing dextrose as weak reducing agent and the resistivity of the silver patterns at 150 °C for 1 h was 24.7 μΩ·cm. Walker et al. [16] reported reactive silver ink with ammonium hydroxide as a complexing agent and formic acid as reducing agent, the electrical conductivity of the silver film equivalent to bulk silver at an annealing temperature of 90 °C. Wu et al. [17] proposed a new silver ink system by using 1-dimethylamino-2-propanol as both the protecting and reducing agent, and silver conductive lines with a

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Table 1
Properties of various amines and the sheet resistance of silver films cured at 150 °C for 10 min from various inks.

Material	Ethylamine	Propylamine	Butylamine	Hexylamine	Ethanediamine	1,2-diaminopropane
Viscosity (mPa·s)	2.46	2.94	3.51	4.11	5.32	4.55
Sheet resistance (Ω/sq)	0.231	0.182	0.114	0.056	0.126	0.055
Boiling point (°C)	16.6	48–49	78	126–132	116–117	120.5
Temperature of decomposition (°C)	190	190	125	130	150	120
Ink pH	13.05	13.13	13.52	13.80	12.10	12.31
Alkyl chain length × amine	2 × 1	3 × 1	4 × 1	6 × 1	2 × 2	3 × 2
FWHM (111) (°)	0.421	0.322	0.168	0.156	0.152	0.149

resistivity of 13.7 μΩ·cm were fabricated at 100 °C for 1 h. A silver-ethylamine-ethanolamine-formate-complex based transparent ink was formulated by Vaseem et al. [19], eight layers cured at 150 °C for 30 min demonstrated conductivities of ~5.2 μΩ·cm. Nie et al. [20] provided an ink synthesized by complexing silver citrate with 1,2-diaminopropane, and the silver films cured at 150 °C for 50 min had a resistivity of 17 μΩ·cm. Wu et al. [21] found that the addition of longer-chain carboxylic acid to the silver ink improved the continuity of the resulting silver film, leading to significantly increased conductivity. The silver film added undecenoic acid showed the lowest resistivity of 43.1 μΩ·cm. Silver MOD ink with high silver content could be facilely prepared by formulating the ink using a low molecular silver salt, and the resistivity of the printed patterns cured at 150 °C for 30 min was 8.6 μΩ·cm [22].

Although previous research works on MOD inks have achieved profitable results, and the properties of the inks have been improved from various aspects by a number of researchers, the developed inks are still far from meeting all the requirements for an ideal MOD ink. Moreover, previous research works had been performed mainly focusing on optimizing a specific MOD ink formulation. The role of each constituent played in the ink formulations has been rarely addressed. Both previous published work and our recent research suggested that the conductivity of silver films is closely related to their microstructure features, which, to a large extent, is determined by the ink formulation [10–22]. Clearly, in order to optimize MOD ink formulation with respect to their ability to be cured at low temperatures and to obtain highly conductive patterns, it is essential to elucidate the roles played by each constituent in the ink system.

We are interested in designing silver MOD inks based on a fundamental understanding of the roles played by each constituent in the ink system. A systematic research has been performed to establish the relationship between microstructure evolution of the cured silver films and the formulations of the inks. As first part of a series work, in this paper, we report on the effects of amines on the properties of the inks. We demonstrated that controlled microstructural features leading to highly conductive silver films could be achieved by proper selection of the kinds of amines. The underlying mechanism was elucidated. Our research work may also provide insight into endeavors aimed at developing MOD inks of other metal ink systems.

Table 2
Properties of silver inks at various Ag/NH_2 molar ratios.

Ink	A1	A2	A3
Silver tartrate (mol)	0.01	0.01	0.01
1,2-diaminopropane (mol)	0.03	0.05	0.07
Ethyl alcohol (mol)	0.1	0.1	0.1
Ag wt%	20.65	18.09	16.10
Ag/NH_2 molar ratio	1:3	1:5	1:7
Viscosity (mPa·s)	5.90	3.95	1.07
Contact angle (°)	22.5	31.6	48.2

2. Experimental details

2.1. Materials

Silver nitrate ($AgNO_3$) was purchased from Sino-platinum Metals Co. Ltd. Sodium tartrate ($C_4O_6H_4Na_2$), ethylamine (C_2H_7N), propylamine (C_3H_9N), butylamine ($C_4H_{11}N$), 1,2-diaminopropane ($C_3H_{10}N_2$), and ethyl alcohol (C_2H_6O) were purchased from Sinopharm Chemical Reagent Co. Ltd. Hexylamine ($C_6H_{15}N$) and ethanediamine ($C_2H_8N_2$) were purchased from Aladdin Industrial Corp. All the reagents were analytical grade and used as received without further purification. Polyethylene terephthalate film (PET) used as substrates in this study were purchased from Du Pont.

2.2. Preparation of silver inks

The silver MOD inks used in this study were prepared by dissolving the synthesized silver tartrate into different amines. Silver tartrate was synthesized in deionized water via an ion-exchange reaction. Amines with different alkyl-chain lengths were used as complexing agents. All the silver inks were formulated by mixing amines, ethyl alcohol (EA) and silver tartrate at 0 °C for 1 h, then the inks were filtered through 0.22 μm syringe filter and directly used for the following experiment. The weight of silver tartrate and ethyl alcohol added to each ink was the same and the Ag/NH_2 molar ratios were kept at a constant value of 1:4 otherwise mentioned.

2.3. Preparation of silver conductive films and conductive lines on PET substrate

The 2 cm × 2 cm PET was used as the substrate for ink property characterization. The PET substrate was cleaned with methanol and deionized water to remove the particles and organic contaminants on the surfaces, and was used for experiment. The silver inks listed in Table 1 were patterned on the substrates by a rod coating method and heated on the hot plate at 150 °C for 10 min, then naturally cooled down to

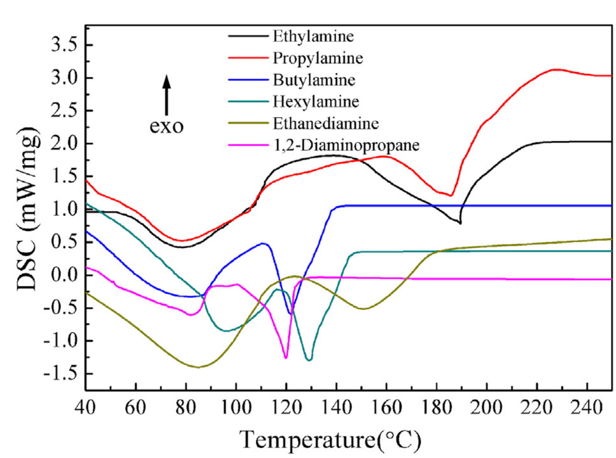

Fig. 1. DSC curves of the inks formulated with various amines.