Chemical Engineering Science 190 (2018) 40–47

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Dual effects of water on the performance of copper complex conductive inks for printed electronics

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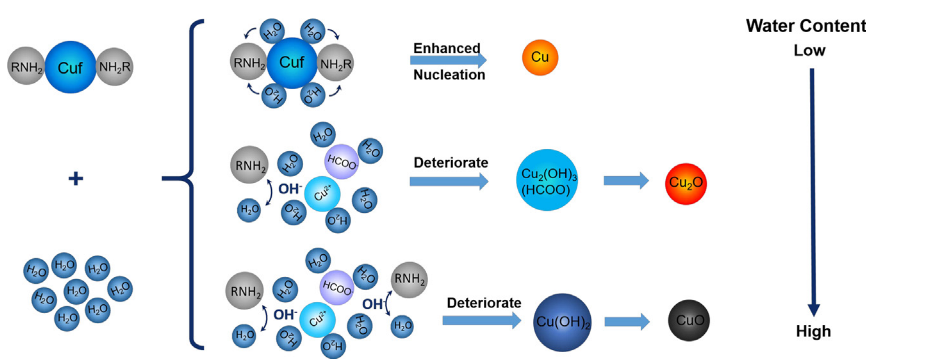
HIGHLIGHTS

- The dual effects of water on copper complex conductive inks were investigated.
- Excess water causes the deterioration of copper complexes inks.
- Trace water promotes copper nucleation to form copper film with lower resistivity.
- A novel ink was developed for long shelf life and high conductivity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 October 2017
Received in revised form 1 June 2018
Accepted 3 June 2018
Available online 4 June 2018

Keywords:
Copper complex
Conductive ink
Water content
Shelf life
Copper film
Electrical resistivity

ABSTRACT

Copper complex conductive inks inevitably contains water which is derived from chemicals and humid air. The dual effects of water on the performance of copper complex conductive inks with amines as ligands were investigated for the first time. On one hand, excess water caused the deterioration of copper complexes by interacting with amines to produce high concentration of OH^-, yielding basic salt, hydroxide or oxide precipitate, which shortened the shelf life of copper inks. The degree of deterioration was related to the amine's coordination ability and alkalinity. On the other hand, trace water could accelerate the thermal decomposition of copper complexes, promote the nucleation of copper, and yield smaller particles to form copper films with denser structure and lower resistivity. The blending of 2-ethylhexylamine (EtHex) and 2-amino-2-methyl-1-propanol (AMP) as ligands to copper formate (Cuf) could balance the dual effects of water on copper complex conductive inks. It was found that Cuf-EtHex-AMP (with 95 mol% EtHex in blended ligands) ink showed strong water resistance. The shelf life of the blended complex ink with additional 2 wt% water was still more than 2 months. The additional water enabled the formation of highly conductive copper films at low heating temperature. The resistivity of the copper film from the blended complex ink with additional 2 wt% water stored for 2 months only increased a little compared to that from the newly prepared ink (from 9.70 μΩ·cm to 14.42 μΩ·cm), which could meet the general requirements of printed electronics.

1. Introduction

The increasing commercial demand for electronics with high quality and low cost pushes the innovation of more efficient fabrication techniques. Printed electronic technology is a promising

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https://doi.org/10.1016/j.ces.2018.06.012
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method for the mass production of cheap, large-area, flexible and wearable electronics, which improves the utilization of raw materials and mitigates environmental pollution (Araki et al., 2013; Cho et al., 2016; Yong et al., 2015). Compared to other printing methods, such as screen printing, flexographic printing and gravure printing, inkjet printing is flexible and contactless, realizing the highly selective patterning on various types of substrates with little loss of materials (Jeong et al., 2011; Kamyshny, 2011; Wang et al., 2013). The development of suitable solvent-based conductive ink is one of the major tasks for the application of inkjet printing.

Copper possesses fairly low electrical resistivity (1.72 μΩ·cm), which is only 1.08 times of silver (1.59 μΩ·cm), but its price is only 1% of silver. Thus the copper based conductive ink is more suitable to fabricate printed electronics with low cost but high quality. Nano copper ink and copper complex ink are two types of the copper based inks. Copper complex ink, also called copper MOD (metal-organic decomposition) ink, can be easily prepared by the coordination of copper salt and ligands, avoiding the complicated preparation of nanoparticles. This particle-free ink can be easily cleaned up by its solvents and won't block the printer's nozzles. Cu ion can be reduced into metallic copper by thermal decomposition through a ligand-to-metal charge transfer (LMCT) process after printing (Shin et al., 2014), overcoming the oxidation and aggregation problems of the nano copper ink. Hence the copper complex ink has aroused the researches' interest. The use of copper formate (Cuf) as copper source together with various types of alkylamines (Choi and Hong, 2015; Xu and Wang, 2017; Yabuki et al., 2011; Yabuki and Tanaka, 2012) or aminediols (Farraj et al., 2015; Shin et al., 2014; Yabuki et al., 2014; Yonezawa et al., 2016) as ligands is a common choice to form copper complex inks. Cuf can be reduced into metallic copper by thermal decomposition with no organic residues (Kim et al., 2012). The complexation of Cuf and alkylamines/aminediols can decrease the decomposition temperature and increase the solubility in alcohols solvents.

In practical use, copper complex conductive inks should not only yield conductive copper films in mild condition with low electrical resistivity and strong adhesion, but also have long shelf life to meet the storage requirements. Till now, most of the studies concentrated on the enhancement of conductivity (Farraj et al., 2017; Lee et al., 2014; Paquet et al., 2016) and the adhesion of the copper film (Choi et al., 2012; Li et al., 2017). The decomposition mechanism of the copper complex and the effects of the ligand's type (Yabuki et al., 2011), concentration (Choi and Hong, 2015; Kim et al., 2012), and alkyl chain length (Xu and Wang, 2017) on copper film formation were also investigated to provide guidance to the design of copper complex inks. In most studies, Cuf tetrahydrate was used as copper source directly, and hygroscopic amines and alcohols were used without purification, which introduced plenty of water into the inks (Choi and Hong, 2015; Farraj et al., 2015; Kim et al., 2012; Shin et al., 2014; Yabuki et al., 2011; Yonezawa et al., 2016). However, the effects of water haven't drawn enough attention. Only Farraj et al. (2015) speculated that water contributed to the complete decomposition of the organic content of Cuf-AMP, which led to the higher conductivity of the printed patterns. Besides, water seems to harm the stability of the inks. Shin et al. (2014) observed that precipitate occurred when Cuf-AMP was dissolved in water. Yonezawa et al. (2016) found that solid materials with light blue color appeared in the liquid Cuf-DEAE (derived from Cuf tetrahydrate and 2-diethylaminoethanol) in a few hours. However, there's no in-depth study to clarify the roles of water.

In this study, we chose several common ligands, namely butylamine, hexylamine, octylamine, 2-ethylhexylamine and 2-amino-2-methyl-1-propanol, to investigate the dual effects of water on the performance of copper complex inks, including shelf life and copper film formation. It was found that excess water was harmful for the preservation of copper complex inks, and the influence was related to the coordination ability and alkalinity of the ligand. However, trace water bonding to copper complex was conducive to the formation of the copper film with denser structure and better conductivity. A novel conductive ink formulation was proposed to balance the dual effects. The prepared conductive ink with additional 2 wt% water could be stored for at least two months, and still yield highly conductive copper film at low heating temperature.

2. Experimental section

2.1. Chemicals and materials

Copper formate tatrahydrate (Cuf tatrahydrate for short, 98%) and 2-ethylhexylamine (EtHex for short, 99%) were purchased from Alfa Aesar. Hexylamine (Hexyl for short, 99%) and octylamine (Octyl for short, 99%) were purchased from Aladdin. Butylamine (Butyl for short, 99.5%) and 2-amino-2-methyl-1-propanol (AMP for short, 98%) were purchased from J&K Scientific Ltd. Ethanol (99.7%) was purchased from Tong Guang fine chemicals company.

Cuf tatrahydrate was dried at 0.001 MPa, 90 °C for 12 h, using P_2O_5 as the desiccant to obtain anhydrous copper formate (Cuf). Amines and ethanol were dried with 4 Å molecular sieves to reduce the water content below 100 ppm.

2.2. Synthesis of copper complex ink and conductive film

The copper complex ink was prepared as follows. The molar ratio of Cuf and ligand was fixed to 1:2. First, the ligand was dissolved in ethanol with variable amounts of deionized water. Then Cuf was added into the solution and stirred at 35 °C for 20 min, forming the deep blue copper complex ink with 9.7 wt% Cu^{2+} content.

As for the control experiments, the copper complex ink using Cuf tatrahydrate and amines without purification was prepared by the similar procedure.

The copper complex without solvent was obtained by drying the ink at 0.001 MPa, 45 °C for 12 h. To get the complex containing 2 wt% water for TG-DSC analysis, the ink synthesized with purified chemicals was dried first, and then mixed with additional deionized water for 8 h vigorously.

To obtain the conductive copper film, 100μL ink was dropped onto the polyimide film (3cm × 3 cm) and spread out on the whole surface with a pipette. Then the ink-coated substrate was dried to remove the ethanol and heated in a tube furnace under N_2 atmosphere.

2.3. Characterization

The water content of the liquid chemicals and Cuf was measured by a Karl Fischer titrator (C20, Mettler-Toledo) and a halogen moisture analyzer (HB43-S, Mettler-Toledo) respectively. The crystalline structures of the precipitates were identified by X-ray diffraction (XRD, D8 Advance, Bruker) using Cu Kα radiation (λ = 1.5406 Å). A Fourier transform infrared spectrometer (FTIR, Tensor 27, Bruker) was used to analyse the chemical structures of the copper complexes and the precipitates. The thermal decomposition behaviors of the copper complexes, Cuf and the precipitates were investigated by the coupling of thermogravimetric analysis and differential scanning calorimetry (TG-DSC, Netzsch, STA 409PC) at the heating rate of 5 °C/min under N_2 atmosphere. The chemical state of the copper films was investigated by X-ray photoelectron spectroscopy (XPS, Esca Lab 250Xi, Thermo scientific) with Al Kα radiation, and the energy calibration was achieved by setting the