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Copper inks with short carbon chain organic Cu-precursors formed in process

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Based-Cu printing inks (20wt% Cu) and (9.6wt% Cu) were prepared using the short carbon chain organic Cu-precursors formed during the preparation of the inks, which can easy form a favorable conductive film onto
5 glass slides at 290℃ and 220℃. The resistance of the film induced by the oxidation of Cu and remainder of long carbon chain Cu-precursors markedly decreased, than usual. The influence factors on the formation and conductive mechanism of the copper ink and film were
10 discussed.

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1. Introduction

Printable conductive inks have attracted much attention due to the potential application in low-cost and sophisticated electronic devices, components and integrated smart systems.[1-7] Conductive inks that can be patterned by silk-screen printing, inkjet printing, or other printing methods to form conductive tracks are a critical component of printing electronic technology.

Up to now, conductive polymer,[8] carbon,[9, 10] graphene[11], and metallic inks[12-19] have been used in the formation of conductive tracks. Among these, silver inks are currently favored inks and rapidly developing. However, high cost, low content, as well as electromigration issues limit wide industrial application of silver inks.

Copper is a good alternative material for silver due to its low cost, good conductivity, and reduced electromigration effect. Various methods to synthesize copper nanoparticle (Nps) inks have been developed[20-26]. However, most of them are not economically feasible because of the low throughput and serious agglomeration. Besides, it is very difficult to obtain pure copper Nps, because the reduction of Cu salts tends to stop at Cu_2O stage and copper Nps can easily be oxidized in air. The presence of copper oxides will increase the sintering temperature of Nps and decrease conductivity. Moreover, the preparation of the Nps inks generally involves in the complex process with toxic organic solvents and poor dispersion stability of copper Nps.

To overcome these problems, organic copper decompositon inks are being intensively researched[27-31], where Cu-precursors are generally mono- or di-valent Cu-organic compounds, and there is no the trouble of the oxidation during the preparation and storage. However, three distinct shortcomings of the inks make them hard to apply commercially, at present. First, most of them require reduction atmosphere (such as hydrogen gas or formic gas), or a special sintering method (intense pulsed light or laser) to make the ink tracks conductive, which induces cost and safty problems and should be avoided for industrial production. Second, the inks generally use nonpolar solvents rather than alcohol species, which could lead to damage on blanket layer[30] and froward compatibility with mass

production technique, especially reverse offset printing. Third, the preparation process is generally complex, and using long carbon chain Cu-compounds as a precursor, which will induce low metallic loading and ill conductivity. To increase the metal load of ink, Lee et al[29] prepared the copper ink by mixing copper (II) neodecanoate and copper hydroxide nanopowder, and annealed the ink trackce under the atmosphere of 3 % H_2 in order to reduce copper hydroxide. And the thermal decomposition ink of amine complexes of copper formate[27, 30, 31] was an innovation to organic copper inks, but this is only example of the ink system, so far. The design and fabrication of well-modulated Cu-inks is still a huge challenge. Specially, it is very pressing to economically develop feasible processes to produce alcohol-based copper inks with short carbon chain organic copper compounds.

In the present work, we designed and prepared two alcohol-based organic copper inks of Ink_{20} (20wt% Cu) and $Ink_{9.6}$ (9.6wt% Cu) with short carbon chain organic copper compounds from the semifinished product during the preparation of the inks. The influence factors on the formation and conductive action of the copper ink and film were discussed.

2. Results and discussion

2.1 Ink_{20}

Ink_{20} was prepared used copper glycolate as a Cu-precursor, which derived from the neutralization reaction of hydroxyacetic acid and copper hydroxide. The obtained copper glycolate powder was redispersed in the mixed solvent of terpineol and lactic acid(1%), then ultrasound for an hour to get the ink (supporting materials).

As an important component of the ink, the characteristic of the copper glycolate was investigated by FT-IR spectra, XRD, SEM and EDS (Fig.S1, Fig.S2, Fig.S3 and Fig.S4) in supporting materials), DSC and TG (Fig.1) to confirm the purity, structure and decomposition temperature of the copper glycolate.
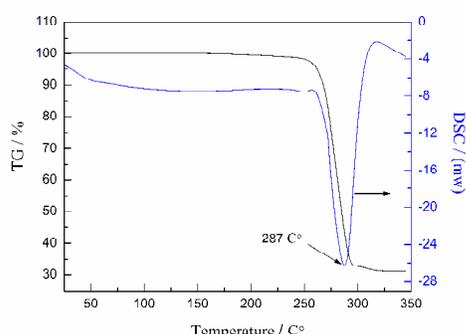
Fig.1. DSC and TG analysis of copper glycolate

The endothermic peak in Fig.1 appeared at about 287℃, where the total loss weight was 68%, implied the leftover copper 32%, which was supported by the XRD spectra in Fig.3. The result is much better than the best one ever reported

(14.2%)[29], where copper neodecanoate was as a metal precursor and got a conductive film under hydrogen atmosphere.

The design and selection of solvent compositions are crucial to ink properties, and should meet various requirements. In the present work, terpineol was used as a high boiling point solvent to suppress the so-called coffee ring effect[18] and solidify the wet film. A given amount of hydroxyacetic acid to improve the adhesion of the ink with the substrate and properties of the copper ink films. As expected, the sintered film with an average thickness of $1\pm0.2\mu m$ had relatively uniform surface structure, where the Cu Nps accumulated at the centre and the 'coffee ring effect' was effectively suppressed (Fig. 2).
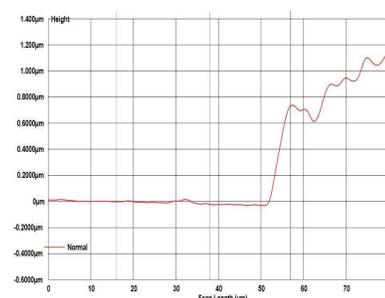
Fig.2. Surface profiles of the copper film deposited on glass after sintering at 290℃ for 60min under nitrogen atmosphere.

Based on the surface profiles observation and sheet resistance measured results of the film (sintered at 290℃), the resistivity calculated was about 3.85×10^{-5} $\Omega\cdot cm$ (Fig.S5).

The XRD spectra of the sintered copper film in Fig.3 are in agreement with the values of a face-centered cubic (fcc) crystal structure of copper. No diffraction peaks from any other impurities were detected, indicated the copper glycolate was directly transformed to copper crystals at 260℃.
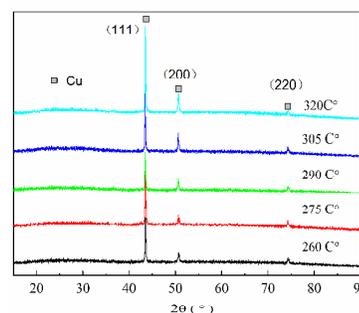
Fig.3. XRD spectra of the copper film sintered at different temperatures

The intensity of the diffraction peaks increased with the sintering temperature, meant the crystallization of Cu Nps become well. As mentioned above, copper is easily oxidized into either Cu_2O or CuO. However, the copper in the sintered copper films here showed stable FCC copper crystal phase, and significantly oxide-free, which may be attributed to the reduction action of a few amount of hydroxyacetic acid:

$$Cu_2O + OHCH_2COO \xrightarrow{\Delta} Cu(s) + H_2O(l) + CH_3COOH(l)$$
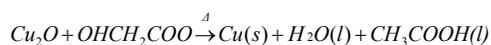
The SEM images of resulting films sintering at different temperature were given in Fig.4. Combination with the SEM image of the copper glycolate (Fig.S3) and the study about thermal decomposition of copper carboxylate (Ref.28), It can be deduced that the films underwent simultaneously the process of evaporation of the coated solvent, decomposition of copper glycolate and neck connecting of produced copper Nps during the sintering. As Fig.4 showed, at lower sintering temperature (260℃), copper glycolate decomposed slowly and formed relatively big particles with less connection among the particles, so the resistivity of the films was bigger. With the increase of temperature (290℃), the copper NPs changed uniform and contacted better with each other, and the film was smooth. Meanwhile, pores and voids among the NPs became less, stacking density was improved greatly, thus, the resistivity gradually decreased. A heat-treatment at higher temperatures (320℃) could further compact the film but the resistance of the film decreased much slowly.
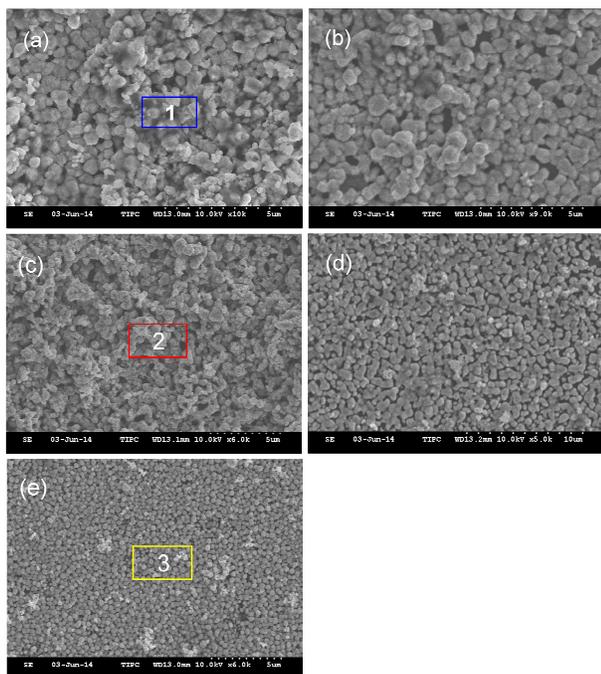
Fig.4. SEM images of the copper films formed at different sintering temperatures for 60min: a. 260, b.275, c.290, d.305, e.320℃. The selected area is for the measurement of Fig.S6.

The chemical composition of the copper film sintered at different temperature was identified by surface energy disperse spectrometer (Fig.S6). Three elements (C, O, and Cu) were detected in the films. With increasing temperature from 260℃ to 320℃, the content of Cu increased from 80.47 wt% to 90.88 wt% and the content of C decreased from 14.98 wt% to 3.37 wt%, indicated the copper glycolate almost fully decomposed and volatilized, and the small quantity of O may be from the residual organic molecules. Considering the copper Nps at high

temperature easy to be oxidized, 290℃ was selected as an optimum sintering temperament.

Briefly, the decomposition degree of copper glycolate, remnant degree of organic molecules at the interface of copper particles and the stacking density of copper Nps are the three dominant factors for the conductivity of sintered copper films.

2.2 Ink$_{9.6}$

In order to further optimize preparing system, we designed a new complexation-reduction process of copper acetate and cyclohexylamine together with formic acid to prepare Ink$_{9.6}$ (supporting materials). The as prepared ink was limpidity and had no particles or any impurities, therefore, meets the request of dispersion stability and antioxidation.

Herein, the lone pair electrons on the nitrogen of cyclohexylamine can coordinate with copper acetate and form copper organic complexes:

$$Cu(CH_3COO)_2 + C_6H_{11}NH_2 \rightarrow [Cu(NH_2)_2]^+[(CH_3COO)_2]^-$$
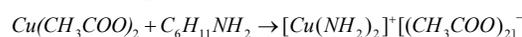
Formic acid were added for Cu ions reduction and stabilization. Ethylene glycol was used as a co-solvent with a high boiling point to suppress the coffee ring effect. Ethanol was used to adjust the surface tension of the ink.

As DSC-TG in Fig.5 showed, the endothermic peak appeared at around 127℃ and 170℃, indexed to the evaporation of amine and ethylene glycol. The exothermic peak at about 200℃ might be from the coalescence of Cu Nps and partial decomposition of organic species. The total loss weight was 85%, implying that the remaining 15% was the copper. And 220℃ was the optimum sintering temperature.
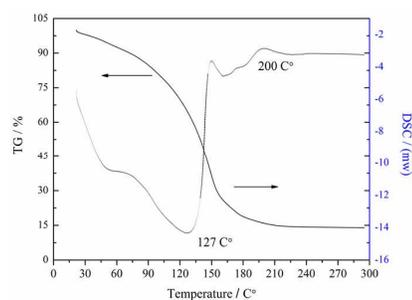
Fig.5. DSC and TG analysis of Ink$_{9.6}$

XRD pattern of the sintered copper film of Ink$_{9.6}$ is well in agreement with the values for a face-centered cubic (fcc) crystal structure of copper. No diffraction peaks from any impurities were detected (supporting materials Fig.S7), indicated the copper Nps were produced. Comparation with previous research results of the thermal decomposition of copper-amine complex[33-35], the following reaction was suggested :

$$Cu(NH_2)_2(CH_3CO_2)_2 + HCOOH \xrightarrow{\Delta} Cu(s) + NH_3(g) + CO_2(g) + H_2O(l) + CH_3COOH(l)$$
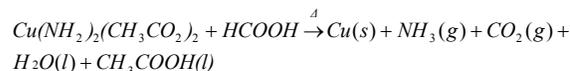
And the uniformity, smooth, and compactness of the sintered films become better, using a mixed solvent (Fig.S8). Two elements (C 4.52 wt% and Cu 95.48 wt%) were detected in the

films (Fig.S8), indicating organic solvent volatilized mostly, a little C may be from the residual organic species.

Based on the SEM observation, we choose the film with an average thickness 1.5μm for the calculation of the resistivity (supporting materials), the resistivity was about $7.5×10^{-5}$ Ω·cm.

Significantly, although the ink contained only 9.6wt % copper, it still offered a delightful conductivity.

It has been found that formic acid was the most critical factor decided the conductivity of the film. The experiments showed, a little formic acid could not influence the reduction of copper ions; but much excess acid would react with cyclohexylamine and produce compounds hard to decompose at lower temperature, and lead to ill conductivity of the sintered film. The optimum molar ration of formic acid and copper acetate was 2:1, according to our experiences.

In the present work, we only use cyclohexylamine in the complexation reaction. However, the types of amine groups are a key factor to the thermal decomposition temperature of copper film[31]. The appropriate amine complexes could significantly decrease sintering temperature and make inks usable on plastic substrates, which need further experiments in the following efforts.

Conclusions

Two kinds of organic copper conductive ink were prepared using the short carbon chains organic Cu-precursor produced by the facile praperation process of the inks. Both of them have good conductivity after sintering, which is comparable to other copper-precursor-based inks[27-31].

As the prepared organic copper decompositon ink, Ink_{20}, using copper glycolate as a precursor, avoided the issue of low metallic loading and bad conductivity from long carbon chain copper precursors as usal and easy formed a favourable conductive film onto glass slides.

The design and praperation of $Ink_{9.6}$ developed a new self-reduction ink system and obtained a pure copper film with a desirable conductivity after simply sintering at 220℃ in ambient atmosphere.

Notes and references

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