

Electrical, Microstructure and Rheology Properties of the Low-Curing-Temperature Silver Paste with Different Carbon-Chain Type Metallo-Organic Salt Wetting Coating

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Abstract

In this paper, the low temperature curing and high conductivity behaviors of silver films using silver paste with metallo-organic salt $C_nH_{2n+1}COOAg$ compound additions are investigated. The low curing temperature silver paste made from flake silver powder, solvent terpeneol and various carbon-chain types of metallo-organic decomposition (MOD) compounds wetting coating on flake silver powder, were prepared and characterized. The microstructures and resistivities of cured films screen-printed from the pastes were examined. The printable and paste rheology were detected using dynamic rheometer. The metallo-organic silver salt decomposition left almost pure and nano silver particles on the flake silver powder surface, which is beneficial for bridging between silver flake powder in the films. The carbon-chain length of metallo-organic silver salt were influenced the decomposition temperature, viscosity and rheology behavior of paste and dissolving behavior by molecule polarity.

The different carbon-chain length metallo-organic silver salts were synthesized from organic acid with $AgNO_3$. The metallo-organic silver salt of synthesized were identified by FTIR. Thermal decomposition effects of different carbon-chain metallo-organic silver salt compounds decomposition behavior are evidenced by TGA and the decomposition activation energy E_a calculated analysis. The microstructures of screen-printed films on alumina substrate after thermally treated were characterized and discussed by field-emission scanning electron microscope (SEM). The electrical resistivity properties of the films were measured using four-point probe method at the curing temperature of 200° to 250°C. The results indicate that metallo-organic silver salt compound $C_nH_{2n+1}COOAg$ carbon-chain (n value) must more than 4 were obtained the excellence electrical resistivities, microstructure and rheology characterization.

Keyword

Low-Curing Temperature Silver Paste; Metallo-Organic Salt; Carbon-Chain; Conductivity Pattern

Introduction

Recently, researcher has been tremendous interest in development of low-cost, processing fast, high reliability and disposable microelectronic devices on a flexible substrate such as flexible electronic. And the flexible electronics is emerging as a multidisciplinary research topic with far reaching impact in a number of areas including flat panel

displays, organic electronics, and distributed marco-electronic systems and architectures. To develop the flexible electronics, any components must tend towards the low temperature process, adhesion in polymer-based substrates, low cost and high-speed manufacture, and high performance. Among them, materials with low temperature process and high

electrical conductivity were generally required for many flexible electronics applications, such as, RFID readers and transponders antennas, terminations for high capacitance capacitors, interconnections for organic light-emitting diode (OLED) and organic thin film transistors (OTFT), and printed circuits on conventional polymer-based substrates.

Most commercial conductive pastes designed for various printing processes are formulated using the conducting metal particles dispersed in a resin or solvent. The conductive pastes are mainly classified into two types, namely the firing type conductive paste and resin type conductive paste. The former has glass as binder, which develops conductive film when heated to a temperature ranging from 500 to 900°C. The latter contains a resin as binder and vehicle, which requires only a low temperature curing process to form a continuous film. However, glasses and resins are generally nonconductive, which may hinder the contacts of metal powders and reduce the electron transmission. Recently, there has been a tremendous interest in low-curing-temperature conductive pastes, which have no glass or resin as addition, but manufactured in a low-cost and at high speed for flexible electronic applications.

In the field of material science, metallizations used for the bonding of devices to the substrate and the interconnections between devices are an important part of the material applications, because they have to provide necessary electrical conduction, wetting on the substrate and structure support. Materials with a high electrical conductivity and a low-temperature and high-speed process were generally required for many flexible electronic applications [1,2]. Two approaches were proposed to overcome these obstacles. The first is the use of suspension of metal nanoparticles. The small size results in considerably lower melting point relative to their bulk material counterparts [2]. After printing process, the metallic nanoparticles can subsequently sinter at a plastic-compatible temperature.

The second approach is the use of metallo-organic decomposition (MOD) technology. Bulk conductivity can be achieved at a low temperature by decomposing metallo-organic precursors on various substrates, where the molecular nature of the compounds allows low temperature conversion to the metal. R.W. Vest and coworkers were successfully apply ink jet printing system with silver neodecanoate MOD ink for hybrid microcircuits [3]. The techniques used silver metallo-organic compounds, such as silver neodecanoate MOD compound, with addition of silver flake to immobilize it during melting and decomposition. The MOD-metal flake mixture maintains its configuration during heating, and will decompose to form a well-bonded, well-resolved conductor at a temperature compatible

to polymer based circuit board substrates.

The MOD compounds are pure synthetic metallo-organic compounds that decompose cleanly at low temperature to precipitate the metal as the metallic element or the oxide, depending on the metal and the atmosphere. The organic bonds with metal atom were weaker than the bonds holding the organic moiety together, and can be thermally broken to deposit the metal. The metallo-organic compounds provide the conditions in which the metal powder mixtures were bonded together with nanoparticles after heat treatment to form well-consolidated conductors. The MOD-metal flake mixtures have been applied by screening, stenciling, gravure printing, dispensing, ink jet printing and spin coating or roll to roll process.

A previous study [4] indicated that silver 2-ethylhexanoate ($C_8H_{15}O_2Ag$) possesses a very low decomposition temperature (190.3°C) among the MOD agents, and it forms silver particles to promote linking among silver flake particles. A low-curing-temperature silver paste with 5 wt% silver 2-ethylhexanoate addition possesses shear-thinning and thixotropic properties and a resistivity of 7.8×10^{-6} Ω-cm after being cured at 250°C, which is near the bulk resistivity of silver [5]. Other previous study [6] indicated that MOD silver pastes with partial substitution of silver flake by Ag_2O and AgO enhances the connectivity and packing density of the silver flakes, and thus increases the electrical conductivity of the films. Resistivity of 14×10^{-6} Ω-cm, was achieved for MOD paste with 20wt% Ag_2O additions after being cured at 200°C for 5min.

In this paper, the paste formulations of silver flake with different carbon-chain length MOD compounds were prepared. The different carbon-chain length metallo-organic silver salts were synthesized from organic acid with $AgNO_3$. The metallo-organic silver salt of synthesized were identified by FTIR and remained silver weight percentage measured by TGA analysis. And the thermal decomposition effects of different carbon-chain metallo-organic silver salt compounds decomposition behavior are evidenced by TGA and the decomposition activation energy E_a calculated analysis. The microstructures of screen-printed films on alumina substrate after thermally treated were characterized and discussed by field-emission scanning electron microscope (SEM). The electrical resistivity properties of the films were measured using four-point probe method at the curing temperature of 200° to 250°C.

Experimental

Commercial available silver flake (Ferro Corp., OH, U.S.A.) was used throughout this study. The different carbon-chain length metallo-organic

compounds $C_nH_{2n+1}COOAg$ including $n=5, 7, 9$ and 11 were selected. The different carbon-chain length metallo-organic silver salts were synthesized from different carbon-chain length organic acid mixed with $AgNO_3$. The silver salt was synthesized following a modified procedure, that was described by Teng [7] and similarity with Dearden[8]. Sodium hydroxide in distilled water was slowly added to different carbon-chain length acids in methanol and was stirred at room temperature for 30min. Silver nitrate in distilled water was added to afford a white precipitate of the different carbon-chain length metallo-organic silver salts. The precipitates were collected by filtration, washed with distilled water and methanol and then dried in vacuum.

The metallo-organic silver salt of synthesized were identified by FTIR and remained silver weight percentage measured by TGA analysis. Various pastes were prepared according to the formulations 80wt% Flake Ag powder, 5wt% metallo-organic silver salt, and 15wt% solvent. The mixtures were mixed by high speed mixer (Thinky Mixer, Japan) for 3 min and then de-bubbled for 1min. Subsequently, uniform pastes were formed through a triple roller grinding (EXERT, Germany), which causes breaking down of the pigment agglomerates.

Thermo-gravimetry analyzer (TGA) from Perkin-Elmer was used at a heating rate of $10^\circ C/min$ in air, to study the variations of the thermal decompose temperature for carbon-chain length metallo-organic silver salts. The TG trace were derivatively calculated to identify the thermal decompose temperatures at which the mass loss of the paste is at a maximum. Also, the TGA were performed at different heating rates including $2^\circ C/min$, $5^\circ C/min$, $10^\circ C/min$, $20^\circ C/min$ and $40^\circ C/min$, in order to evaluate the activation energy. The decomposition activation energy E_a was calculated using the following formula form Doyle-Ozawa [9]:

$$-\log \phi - 0.4567 \left(\frac{E_a}{RT_m} \right) = \text{constant}$$

ϕ is the heating rates (dt/dT) of the measurement and T_m is the thermal decompose temperature of the paste measured.

The rheological measurements of the pastes were explored using a shear stress controlled rheometer (HAAKE RS150) with a plate-plate measuring system (35 mm diameter, gap 0.5 mm). The paste sample were screen-printed on alumina substrate as spiral lines and then thermally treated at a range of temperatures, according to the results of thermal study described above. The dimension of screen-printed spiral silver metal lines are specifically controlled at the length of 216 cm, the line wide of 0.8mm and the line thickness of $20 \sim 40 \mu m$ to promote the accuracy

of the electrical measurement. Keithely 2400 multimeter with a four-point probe was used to measure the bulk resistance of curing silver paste. The resistivity of the silver conducting line cured at the different temperature was calculated using the relationship of $\rho = (R \cdot w \cdot d) / l$. R is the silver conducting line bulk resistance measured, and w, l, d are the width, length and thickness of the silver conducting line, respectively. The microstructures of films cured at various temperatures and holding times were investigated using the SEM (S4500, Hitachi, Japan).

Results and Discussion

The metallo-organic compounds (MOD) provide the conditions in which the metal powder mixtures were bonded together with nanoparticles after heat treatment to form well-consolidated conductors. For the thermal decomposition characteristic, the thermal decomposition temperatures of the pastes were easily identified using the thermo gravimetric analysis (TGA) and derivative thermo gravimetric analysis (DTG). **Figure 1** shows TGA results of the synthesized silver salts of different carbon-chain length metallo-organic compounds $C_nH_{2n+1}COOAg$, the $n = 5, 7, 9$ and 11 . The results indicate that thermal decomposition temperature of $C_nH_{2n+1}COOAg$ ($n = 5, 7, 9$ and 13) is between 239.4 to $263.4^\circ C$ and remained silver weight percentage is 48.9, 39.5, 37.8 and 31.9wt% were conformed to theoretical calculation.

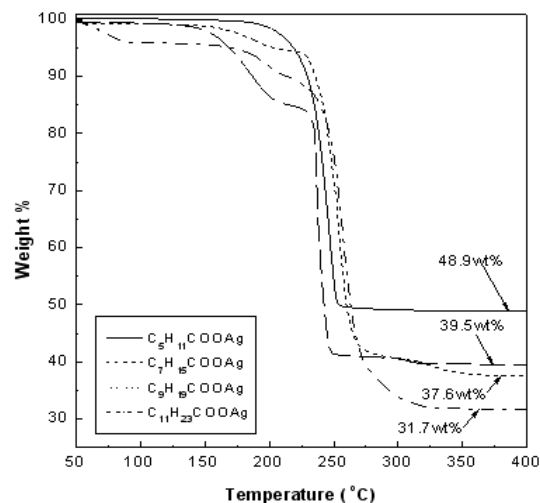


Figure 1. TGA results of the different carbon-chain length metallo-organic compounds.

Figure 2 shows the paste thermal decomposition characteristic of the different carbon-chain length metallo-organic compounds additions. The results indicate that main thermal decomposition were organic solvent decomposition between $150^\circ C$ to

200⁰C, and second thermal decomposition were MOD compounds decomposition including the additions of different carbon-chain length metallo-organic compounds and lubricant coated on silver flakes between 200⁰C to 250⁰C. The organic lubricant was added during mechanical milling for the flaking of silver powder. The lubricant, fatty acid, on Ag flake surface plays an important role for the performance of the paste, including the dispersity of the silver flake in the paste, rheology of the paste, and the electrical conductivity of the paste after curing.

The activations energies of the corresponding decompositions (E_a) calculated from DTG results are shown at **Table.1**. The results shown the activations energies of synthesized silver salts of different carbon-chain length metallo-organic compounds $C_nH_{2n+1}COOAg$, the $n = 5, 9$ and 11 were decreased by increased the carbon-chain length (n value), excluded $n=7$. Consider the carbon-chain length (n value) $n=7$ $C_7H_{15}COOAg$ have coincidence molecules polarity with solvent and lubricant of flake silver powder and the results respond to microstructure after sintering and viscoelastic relaxation time spectrum with rheology measurement. The paste of carbon-chain length (n value), $n=7$, $C_7H_{15}COOAg$ addition have lower thermal decomposition temperature at 235.19⁰C in this study. Other, the organic lubricant was added during mechanical milling for the flaking of silver powder. The lubricant, fatty acid, on Ag flake surface plays an important role for the performance of the paste, including the dispersity of the silver flake in the paste, rheology of the paste, and the electrical conductivity of the paste after curing. However the lubricants sometime were used the silver metallo-organic compounds in the silver paste system.

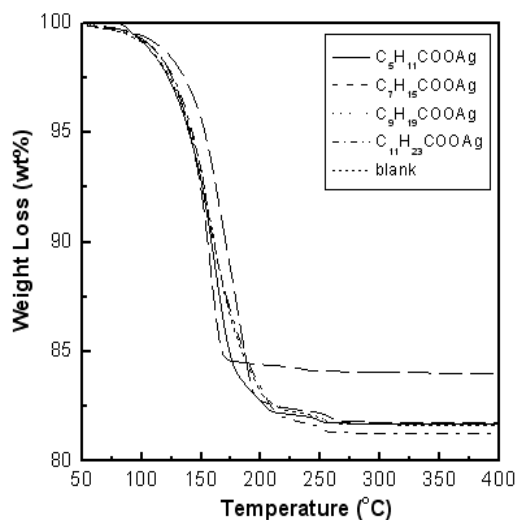


Figure. 2. Paste thermal decomposition characteristic of the different carbon-chain length metallo-organic compounds additions

Table. 1. The activations energies of the corresponding decompositions (E_a) calculated from $C_nH_{2n+1}COOAg$ DTG results

n value	Activations energies E_a (KJ/mole)	$T_m(^{\circ}C)$
5	2307.68	247.59
7	3148.49	235.91
9	2546.59	253.96
11	2527.04	256.50

The viscosities results of the pastes using viscometer with additions of different carbon-chain length metallo-organic compounds were shown in **Figure 3**. It shows that all pastes appear pseudoplastic flow (shear-thinning) property and the MOD additions were increased paste viscosity.

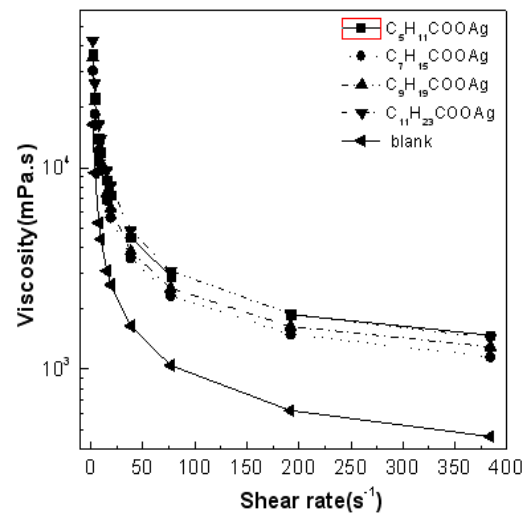


Figure. 3. Viscosities results of the pastes using additions of different carbon-chain length metallo-organic compounds

The results of the viscoelastic relaxation time spectrum of rheology measurement for different carbon-chain length metallo-organic compounds added at shear stress 1 Pa, which indicates the material response to impact or gradual load. The storage G' and loss G'' moduli linearly decrease with decreasing frequency, which indicates that the stress relaxation is very rapid. The $\tan \delta = G''/G'$ reveals the viscoelastic behavior of different carbon-chain length metallo-organic compounds in the paste. The all of the results shown the $G'' > G'$, were appeared the non-associated particle phenomenon for the paste. And the results shown the paste of no metallo-organic compounds and short carbon chain metallo-organic compounds additions were not existed the crosslink point of G' and G'' and shown the short carbon chain length were not affect the viscoelastic of paste. When pastes of another carbon chain length metallo-organic compounds additions ($n=7, 9$ and 11) were obtained the relaxation time 5.49s, 5.74s and 6.47s. And shown

the relaxation time increased with raised the carbon chain length. And the carbon-chain length of metallo-organic compounds were affected the molecules polarity and affected the dissolvable properties for metallo-organic compounds and solvents.

Figure 4 shows the SEM micrographs of low-curing-temperature silver paste with different carbon-chain length metallo-organic compounds added and cured at 250°C for 10min. The **figure 4 (2)** results shown the microstructure when additions of metallo-organic compounds ($C_nH_{2n+1}COOAg$, $n=5$) were reducing lower nano silver particle and aggregated itself. When the additions of metallo-organic compounds ($C_nH_{2n+1}COOAg$, $n=7$) were appeared the larger silver aggregations from metallo-organic compounds decomposition and filling in the intervals between flake silvers and shown at **figure 4 (3)**. When the additions of metallo-organic compounds ($C_nH_{2n+1}COOAg$, $n=7\sim9$) were appeared the larger silver aggregations and some necking phenomenon from metallo-organic compounds decomposition and have high densification structure. However, when increased the n value to 11, 13, show at **figure 4(5, 6)** the necking phenomenon were disappeared and high package density were appeared. Consider the metallo-organic compounds were self-aggregated in the solvent than the size of silver particles thermal reduction were depend on size of metallo-organic compounds molecules and the structure of molecules space effective. The particles package density and necking behavior were induced the electrical conductivity characteristics. And the sintering temperature and dwell time were induced the package state effective by metallo-organic compounds decomposition and structure of molecules space effective and rheology behavior were affected the paste package density and microstructure.

Figure 5 show the resistivity of silver paste with different carbon-chain length metallo-organic compounds additions and cured at different temperatures 175, 200, 225 and 250°C for dwell time 10 min. The metallic silver particles provide the bridging of the silver flake particles and thus increase the conductivity of the metal film. The resistivity results were consistent with SEM results after sintering. The paste additions of metallo-organic compounds $C_nH_{2n+1}COOAg$, $n=7$ and $n=9$ were obtained the lower electrical resistivity and results responded to activations energies of the corresponding decompositions (E_a) and microstructure results. The two kinds conditions of MOD addition amounts were appeared the nano-particle by MOD thermal reductionnechgrowth on flake silver powder surface. And all of the paste were sintering and decreased electrical resistivity at over 200°C. In accordance with the electrical resistivity and SEM results were obtained the carbon-chain length unable to change the

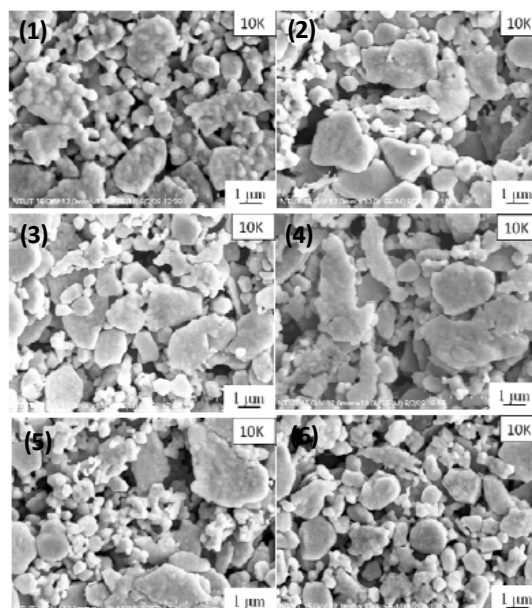


Figure 4. SEM micrographs of paste with different carbon-chain length metallo-organic compounds added and cured at 250°C for 10min.

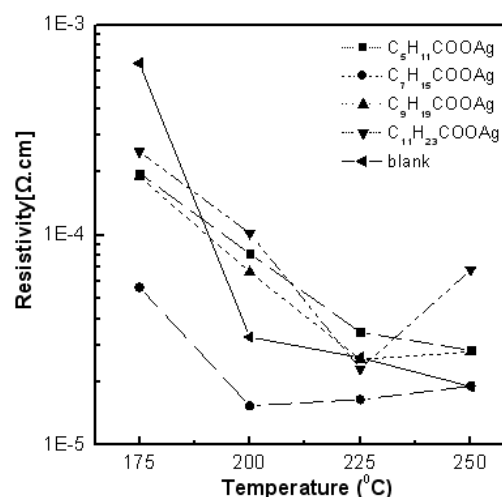


Figure 5. Resistivity of silver paste with different carbon-chain length metallo-organic compounds additions and cured at different temperatures 175, 200, 225 and 250°C for dwell time 10 min.

thermal decomposition temperature and structure densification properties after sintering. However, the molecules structure of metallo-organic compounds was influenced the behavior of adhesion which metallo-organic compounds coated on the flake silver powder in the paste system.

The higher sintering temperature was increased the electrical resistivity of metal films. The sintering neckgrowth behavior and shrinking phenomenon for silver flake powder and nano-particles of reduction

from metallo-organic compound were cut off the electron transmission way to increase the electrical resistance.

Conclusions

The thermal decomposition is the dominating reaction during heating of different carbon-chain length metallo-organic compounds additions in the air. Low-curing-temperature silver pastes from Ag flake powders, solvent and different carbon-chain length metallo-organic compounds additions were prepared. The structure of metallo-organic compounds molecules were affected the adhesion behavior of metallo-organic compounds on the flake silver powder. The metallo-organic compounds $C_nH_{2n+1}COOAg$ additions paste with $n=7$, and 9 is the best formulation studied and higher package density with neckgrowth behavior and low thermal temperature decomposition characteristic, which possesses shear-thinning and thixotropy properties and the resistivity of $15 \times 10^{-6} \Omega\text{-cm}$ after cured at 200°C , which is relatively close to the application electrical resistivity. For the viscoelastic behavior study results shown the paste of no metallo-organic compounds and short carbon chain metallo-organic compounds additions were not existed the crosslink point of G' and G'' and shown the short carbon chain length were not affect the viscoelastic of paste.

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