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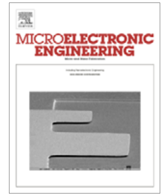

Effects of silver oxalate additions on the physical characteristics of low-temperature-curing MOD silver paste for thick-film applications

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ABSTRACT

In this paper, the effect of silver oxalate addition on physical characteristics of metallo-organic-decomposition (MOD) silver screen-printable paste for thick film technology was investigated. The addition of silver oxalate in the paste not only produces fresh fine silver particles after curing, but also reduces the decomposition temperature of the lubricant coated on the silver flakes. This is an effective route to provide fine silver particles to the paste without significantly changing the rheological behavior. At the curing temperature of 225 °C, the resistivity decreases from 180.1 to 31.9 μΩ-cm, as the silver oxalate content increases from 0 to 10 wt%. This is due to the fact that active silver catalysts produced increase the packing density of silver flakes, and also the removal of lubricant from the surface of silver flakes enhances the electrical conductivity, thereby decreasing the resistance of film.

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1. Introduction

Recently, there has been tremendous interest in the development of low-cost disposable microelectronic devices on a flexible substrate, such as radio-frequency identification (RFID) tags. Metallization used for the bonding of devices to the substrate and the interconnections between devices are critical for the physical performance of the devices. They have to provide necessary electrical conduction, wetting on the substrate and structural support. Materials with a high electrical conductivity and suitable for high-speed processing at a low-temperature were generally required for many flexible electronic applications [1,2]. Among various processing methods, screen printing, electro-photographic printing and ink-jet printing have commonly been used to form precise electrically-conductive patterns by depositing metal particles onto an insulating substrate surface.

Typically, fabricating a conductive layer on substrates requires temperatures less than 350 °C for polyimide substrates, 290 °C for printed circuit boards (PCBs), and 200 °C for other plastics, to prevent any softening or wrapping. Conventional low-temperature electrically conductive adhesives (ECA) have several limitations such as relatively low electrical conductivity and unstable contact resistance. Resistivity of the conductive layer such as silver on the substrate is usually 10–50 times that of pure silver, due to the presence of binding organics, which results in more power consumption and signal loss and thus decreasing transmission distance during signal transmission. These shortcomings can be resolved by the use of metallo-organic-decomposition (MOD) technology. High conductivity can be achieved at a low-temperature by decomposing metallo-organic compounds on various substrates, where the molecular nature of the compounds allows low-temperature of conversion to the metal. The MOD-metal flake mixtures have been applied by screen printing [3–5] and ink-jet printing process [6,7]. Vest and coworkers successfully applied ink-jet printing system with silver neodecanoate MOD ink for hybrid microcircuits [8]. Recently, very low-curing temperature silver inks for use in ink-jet printing were reported [6,7]. The resistivity values of the printed conductive films composed of nano-silver particles, after heat-treatment at 150 °C, were found to have dropped to two or three times the theoretical electrical resistivity of the bulk silver. The ink-jet printable inks usually have a solid loading of less than 20 wt%, a binder content of less than 3 wt% and a viscosity of less than 10 cps.

Also, patent literatures have further revealed the technology of MOD combined with metal flake in screen-printable thick film metallizations and terminations, which are then built up with solder or electroplating [3,4]. These techniques have used silver metallo-organic compounds, such as silver neodecanoate MOD compound, with the addition of silver flakes 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 electrical conductivity is equal to that obtained by conventional thick film conductors sintered at high temperatures (>700 °C).

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A previous study [5] 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 for thick-film applications possesses shear-thinning and thixotropic properties. A resistivity of 7.8×10^{-6} Ω-cm for screen-printed films was obtained after being cured at 250 °C for 30 min, which is close to the bulk resistivity of silver [9]. In this study, attempts to modify the curing conditions of MOD silver screen-printable pastes through the addition of silver flakes by silver oxalate ($Ag_2C_2O_4$) were made. The effect of silver oxalate addition on the thermal properties, rheological behavior and curing conditions of the MOD silver paste were investigated. The microstructure and resistivities of screen-printed films on alumina substrate after being thermally treated were characterized and discussed.

2. Experimental procedure

The low-temperature-curing silver pastes used in this study were prepared from silver flake (Ferro, USA), silver oxalate ($Ag_2C_2O_4$, Rose Scientific Ltd., Alberta, Canada), metallo-organic compound of silver 2-ethylhexanoate (STREM, MA, USA), and solvent of α-terpineol (TCI, Japan). All materials were mixed by a high-speed mixer (Thinky Mixer) for 3 min and degassed for 1 min. Subsequently, uniform pastes were formed using a triple-roller grinder (EXERT, Germany), which causes the breakdown of pigment agglomerates. The weight ratio of silver flake powder and silver 2-ethylhexanoate to solvent was fixed at 81:4:15 (Table 1). Also, 1, 3, 5, 10 wt% of the silver oxalate were added, in order to reduce the curing temperature while still retaining a good conductivity of the resultant film. The silver oxalate powders have average particle size (d_{50}) of 1.7 μm as measured by light scattering (HORIBA LA-910).

Fig. 1. Configuration of spiral silver metal lines screen-printed on alumina substrate for the resistivity measurement.

In order to understand the thermal behavior, the thermogravimetry analysis (TGA; Perkin–Elmer 7) and differential thermal analysis (DTA; Perkin–Elmer 7) were performed in air at a heating rate of 10 °C/min on the pastes as well as pure MOD silver 2-ethylhexanoate and pure silver oxalate. The rheological behaviors of the pastes were explored using a controlled-shear-stress rheometer (HAAKE RS150) with a plate-plate measuring system (35 mm diameter, 0.5 mm gap).

Spiral silver metal lines with a length (l) of 216 cm, a line width (w) of 0.8 mm and a line thickness (d) of 20–40 μm, as shown in Fig. 1, were screen-printed on alumina substrate for the resistivity measurement. A Keithely 2400 multimeter with a four-point probe was used to measure the bulk resistance of cured silver paste. The resistivity of the silver conducting line cured at various temperatures was calculated using the relationship $\rho = (R \cdot w \cdot d)/l$, in which R is the resistance of the spiral. The microstructures of the films cured at various temperatures and holding times were investigated using a field-emission scanning electron microscope (SEM; JEOL-6500F, Tokyo, Japan).

3. Results and discussion

Fig. 2 shows the DTA curves for pure MOD silver 2-ethylhexanoate and pure silver oxalate. The thermal decomposition of silver oxalate occurs at a lower temperature than that of silver 2-ethylhexanoate. It reveals that both reactions are exothermic, which generates a relatively large amount of heat. The silver oxalate shows an exothermic peak at 229.39 °C and the silver 2-ethylhexanoate at 266.25 °C. The reactions are as follows:

$$AgC_8H_{15}O_2 + (43/4)O_2 \rightarrow Ag + 8CO_2 + (15/2)H_2O \quad (1)$$

$$Ag_2C_2O_4 \rightarrow 2Ag + 2CO_2 \quad (2)$$

Previous study revealed that the thermal treatment of $C_8H_{15}O_2Ag$ results in the formation of various organic species including CH_3, CO, O_2, CH_2CO, CO_2, C_4H_9, CH_5COOH, $C_5H_{10}O$, etc., depending on the temperature and the atmosphere [9]. On the

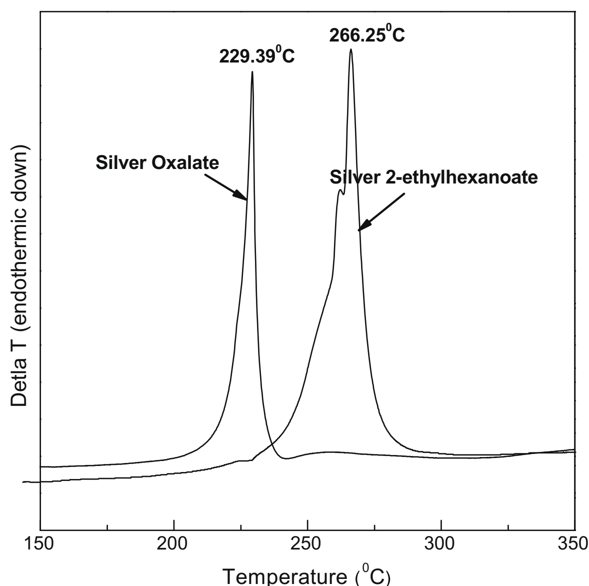

Fig. 2. DTA curves for pure silver 2-ethylhexanoate and pure silver oxalate.

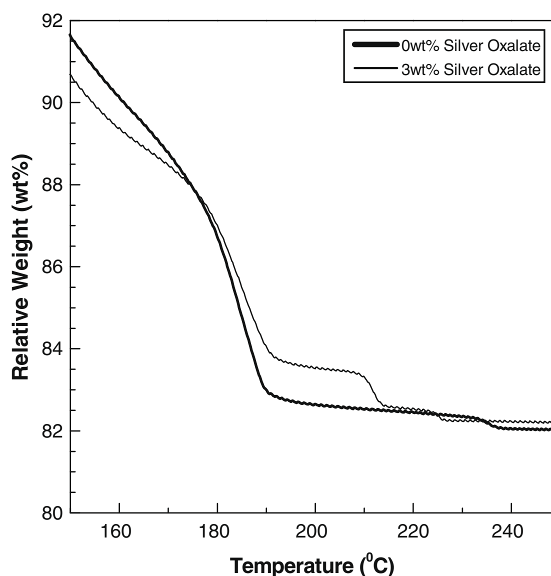

Fig. 3. TGA curves for the pastes with 0 and 3 wt% silver oxalate additions.

other hand, thermal decomposition of the silver oxalate is different from most oxalates that usually decompose to form a metal carbonate or a metal oxide. It gives rise to silver as the solid product and CO_2 as the gaseous product [10]. The decomposition of the silver oxalate produces nearly 71 wt% of fine silver catalyst, which is certainly a good silver source among various MOD compounds. When the silver 2-ethylhexanoate or silver oxalate was mixed with solvent α-terpineol, the former is soluble in the solvent, but the latter is not. Previous study has shown that the decomposition temperatures of silver 2-ethylhexanoate or silver oxalate in α-terpineol are reduced to 190.3 and 212.14 °C, respectively [5].

Fig. 3 shows the results of the thermogravimetric analysis (TGA) for the pastes without and with 3 wt% silver oxalate added in air. For the paste with no silver oxalate being added, the decomposition of the α-terpineol and silver 2-ethylhexanoate lead to a weight loss of 17.26 wt% at temperatures below 190 °C. There is a weight loss of 0.3% observed at ≈235 °C, which corresponds to the decomposition of the lubricant, fatty acid, coated on the silver flakes. For the paste with 3 wt% silver oxalate added, there are three weight drops as the temperature increases from room temperature to 300 °C. Weight loss of 16.76 wt% occurs at temperatures below 190 °C due to the decompositions of α-terpineol and silver 2-ethylhexanoate, 0.87 wt% at ≈210 °C resulting from the decomposition of silver oxalate, and ≈0.3% at ≈222 °C associated with removal of lubricant from the surfaces of silver flakes. The weight losses observed are relatively consistent with the theoretical values calculated from the paste formulations and the chemical formula of the compounds. The results verify that the addition of the silver oxalate not only produces fresh fine silver particles, but also reduces the decomposition temperature of the lubricant coated on the silver flakes.

Rheological characteristics of the pastes with various amounts of silver oxalate being added are shown in Fig. 4. It indicates that all pastes have pseudoplastic flow (shear-thinning) property (Fig. 4a). The solid loading of the paste increases with the silver oxalate content since it is not soluble in the α-terpineol. However, the viscosity of the paste only slightly increases with the content of silver oxalate. Fig. 4b indicates that all pastes possess pseudoplastic flow property with an apparent yield point, which is beneficial to the dimensional control during screen-printing process. The apparent yield point does not vary with the content of silver oxalate. Based on the paste formulations shown in Table 1, the total silver content in the paste slightly decreases from 82.74 to 81.67 wt% as the content of the silver oxalate increases from 0 to 10 wt%. Simultaneously, the ratio of the fresh fine silver particles, decomposed from the silver oxalate and silver 2-ethylhexanoate, would increase from 1.74 to 8.03 wt% of the total paste. This is an effective route to provide fine silver particles to the paste without significantly changing the rheology of the paste. Direct addition of a small quantity of nano-sized silver particles in the paste would significantly increase the viscosity of the paste to an unacceptable value and easily leads to agglomeration of the silver particles.

Fig. 5 shows the SEM micrographs of the films, prepared from the pastes with 0, 3, and 10 wt% of silver oxalate additions, after being cured for 5 min at 225 °C. The films generally contain silver grains with a wide size distribution. They indicate that a higher amount of silver oxalate added produces a higher packing density of film. Fine silver particles, produced from the decomposition of silver oxalate and silver 2-ethylhexanoate, occupied the voids among silver flakes. This will enhance the connectivity of the silver particles in the film, as shown in Fig. 5b and c.

Fig. 6 shows the resistivities of silver films prepared from the pastes with various amounts of silver oxalate added and cured at different temperatures for 5 min. The film resistivity generally decreases with increasing curing temperature, due to a better con-

Table 1
Formulations of the pastes prepared in this study.

Paste no.	Paste formulation (wt%)			Addition of silver oxalate (wt% of paste)	Final paste formation (wt%)				Silver content in paste (wt%)
	Silver flake	α-Terpineol	Silver 2-ethylhexanoate		Silver flake	α-Terpineol	Silver 2-ethylhexanoate	Silver oxalate	
1	81.00	15.00	4.00	0	81.00	15.00	4.00	0	82.74
2	81.00	15.00	4.00	1.00	80.20	14.85	3.96	0.99	82.62
3	81.00	15.00	4.00	3.00	78.64	14.56	3.88	2.91	82.35
4	81.00	15.00	4.00	5.00	77.14	14.28	3.81	4.76	82.17
5	81.00	15.00	4.00	10.00	73.64	13.64	3.64	9.09	81.67

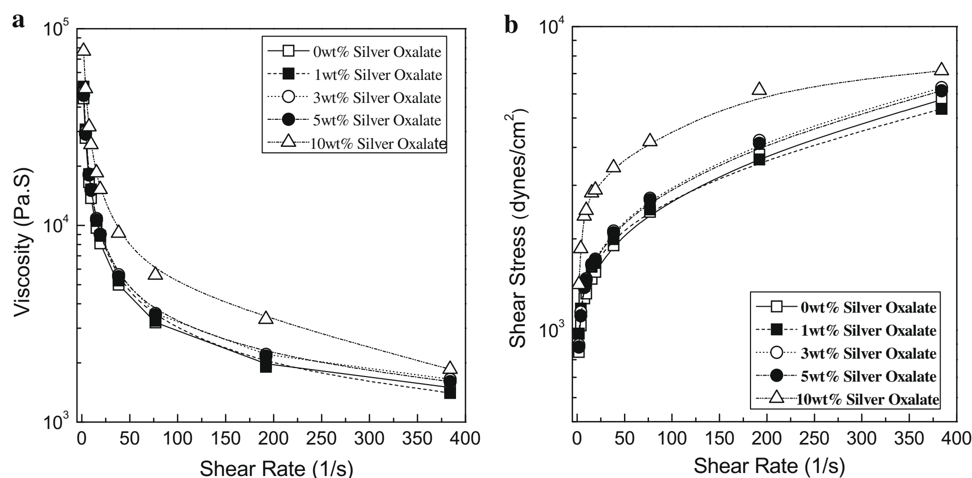

Fig. 4. Rheological properties of the pastes with various amounts of silver oxalate added.

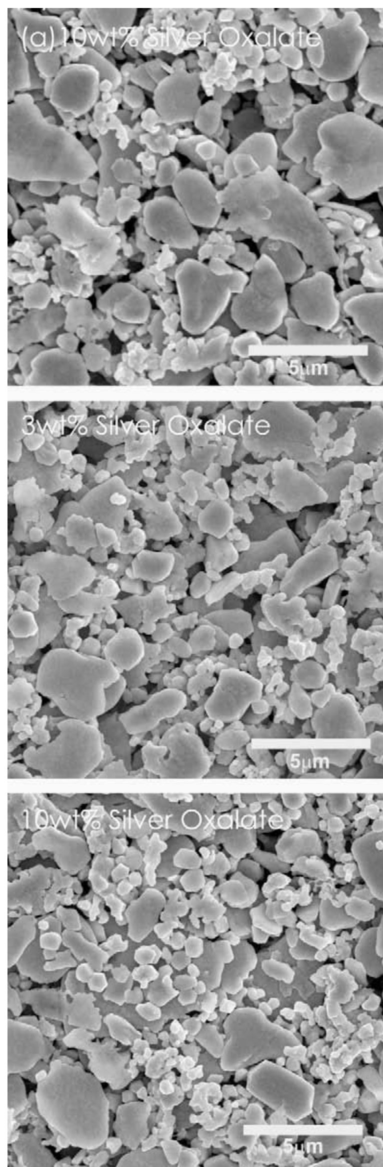

Fig. 5. SEM micrographs of the silver films prepared from the pastes with (a) 1 wt%, (b) 3 wt%, and (c) 10 wt% silver oxalate added and cured at 225 °C for 5 min.

nectivity of the metal particles associated with the decomposition of organics. The resistivity decreases with increasing silver oxalate content for the films cured at temperatures less than 250 °C. At the curing temperature of 225 °C, the resistivity decreases from 180.1 to 31.9 μΩ-cm, as the silver oxalate content increases from 0 to 10 wt%. There are two contributions which are responsible for lowering the resistivity of the films. One is that the content of fresh fine silver particles in the cured silver film increases from 2.10 to 10.17 wt% of the total silver, due to the decomposition of MOD compounds, as the silver oxalate content rises from 0 to 10 wt%. (Table 1). The other contribution is from the addition of the silver oxalate in the paste that reduces the thermal-decomposition-temperature of the lubricant, fatty acid, coated on the silver flakes. The thermal decomposition of silver oxalate and silver 2-ethylhexanoate produces active silver catalysts, which increase the packing density and assist the necking of silver flakes in the films. The removal of the lubricant from the surfaces of silver flakes would increase their connectivity. These would be beneficial to the electron conduction and thus decrease the resistivity of the film. For the curing temperature above 250 °C, the resistivities of the films are

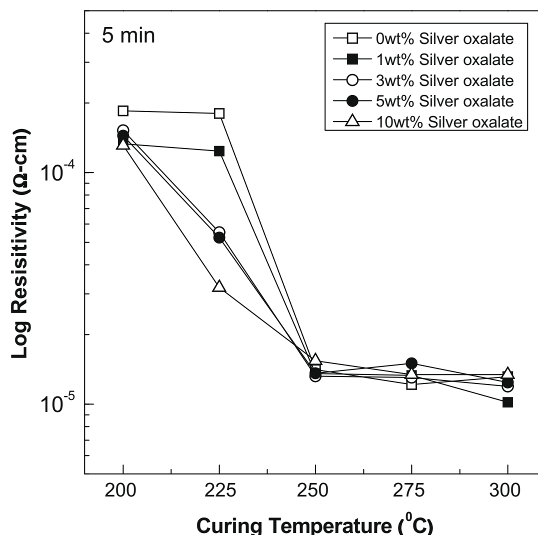

Fig. 6. Resistivities of silver films prepared from the pastes with various amounts of silver oxalate added and cured at various temperatures for 5 min.

very similar and range from 10.18 to 15.03 μΩ-cm, since there are no organic residues left and the connectivity of the silver particles gets to a saturation limit. The resistivity is insensitive to the increasing curing temperature, unless it reaches the sintering temperature of silver particles.

Based on the above results, addition of MOD compounds, such as 2-ethylhexanoate and silver oxalate, not only offers the rheology of the paste required for screen-printing process, but also provides fresh fine silver particles, after decomposition, needed for electronic conduction. Selection of an appropriate MOD compound with a low decomposition temperature in the silver paste is beneficial for use in thick film application, particularly in flexible substrates.

4. Summary

In this study, MOD silver screen-printable pastes with various amounts of silver oxalate being added were prepared. With the addition of silver oxalate, the decompositions of α-terpineol and silver 2-ethylhexanoate occur at temperatures below 190 °C, the silver oxalate at ≈210 °C, and the lubricant on the surfaces of silver flakes at ≈222 °C. The resistivity of the film prepared from the pastes decreases with increasing curing temperature, due to a better connectivity of the metal particles associated with the decomposition of organics. A resistivity of 31.9 μΩ-cm was obtained for the film prepared from the paste with 10 wt% silver oxalate added and cured at 225 °C.

References

[1] D. Redinger, S. Yin, R. Farschi, V. Subramanian, IEEE Trans. Electron Dev. 51 (12) (2004) 1978.
[2] V. Subramanian, J.M.J. Frechet, P.C. Chang, D.C. Huang, J.B. Lee, S.E. Molesa, A.R. Murphy, D.R. Redinger, S.K. Volkman, Proc. IEEE 93 (7) (2005) 1330.
[3] P.H. Kydd, United States Patent No. 6,036,889, 2000.
[4] P.H. Kydd, PCT Patent WO 98/37133, 1998.
[5] C.A. Lu, P. Lin, H.C. Lin, S.F. Wang, Jpn. J. Appl. Phys. 45 (2006) 6987.
[6] A.L. Dearden, P.J. Smith, D.Y. Shin, N. Reis, B. Derby, P. O'Brien, Macromol. Rapid Commun. 26 (2005) 315.
[7] D. Kim, J. Moon, Electrochem. Solid State Lett. 8 (2005) J30.
[8] K.F. Teng, R.W. Vest, IEEE Trans. Compon. Hybrid Manuf. Technol. CHMT-12 (4) (1987) 545.
[9] C.A. Lu, P. Lin, H.C. Lin, S.F. Wang, Jpn. J. Appl. Phys. 46 (2007) 251.
[10] V.V. Boldyrev, Thermochim. Acta 388 (2002) 63.