Chapter 3

Effects of MOD Agents on the Thermal decomposition and the Electrical Conductivity of Low Temperature Curing Silver Paste

Six low curing pastes were prepared from silver flake and α-terpineol and with different metallo-organic decomposition (MOD) compounds. The thermal decomposition behaviors of the pastes were performed. The microstructures and resistivities of screen-printed films on alumina substrate after thermally treated were characterized and discussed. Results indicated 2-ethylhexanoate possesses the lowest decomposition temperature at 190.3°C among the MOD agents studied, which forms silver particles to promote the linking of the flake silver powders and thus reduces the resistivity down to <10μΩ-cm at the temperature as low as 200°C.

3-1 Introduction

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 readersand 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.

Conventional low temperature electrically conductive adhesives (ECA) have several limitations such as relatively low electrical conductivity and unstable contact resistance. 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 [1]. After printing process, the metallic nanoparticles can subsequently sinter at a plastic-compatible temperature. It is therefore possible to produce low-resistance metal lines, thus providing a pathway to realization of high-Q passive components and also to multilevel interconnects on the printed wiring board (PWB) assembly and so on.

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 [2]. Also, patent literatures have further revealed the technology of MOD combined with metal flake powder in thin film metallizations and terminations, which are then built up with solder or electroplating [3,4]. 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 electrical conductivity is equal to that obtained by conventional thick film conductors sintered at high temperatures (>700°C).

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.

Though the technology of MOD-metal flake mixtures has been reported, rare information regarding the physical and chemical nature appear in the literature. In this paper, the paste formulations of silver flake with different MOD compounds were prepared. The behaviors of thermal decomposition were studied. The paste were screen-printed on alumina substrate as spiral lines and then thermally treated at a range of temperatures. The microstructures and resistivities of the resulted films were characterized and discussed.

3-2 Experiment Procedure

3-2-1 Paste Preparation

Commercial available silver flake (Ferro Corp., OH, U.S.A.) was used throughout this study. Metallo-organic compounds including silver 2-ethylhexanoate (STREM, MA, U.S.A.), silver oxalate (Rose Scientific Ltd., Alberta, Canadian), silver stearate (GROTTO, CA, U.S.A.), silver cyclohexylbutyrate (Aldrich, NJ, U.S.A.), and behenic acid silver salt (STREM, MA, U.S.A.), and α-terpineol solvent (TCI, Japan) were selected. The chemical structures of the MOD agents are shown in **Table 3-1**. Various pastes were prepared according to the formulations shown in **Table 3-2**. 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.

3-2-2 Thermal Decomposition Analyze

Thermo-gravimetry analyzer (TGA) from Perkin-Elmer was used at a heating rate of 10℃/min in air, to study the variations of the thermal decompose temperature for low temperature silver pastes with additions of different MOD agents. 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°C /min, 5°C /min, 10°C /min, 20°C /min and 40°C /min, in order to evaluate the activation energy. The decomposition activation energy E_a was calculated using the following formula form Doyle-Ozawa [5]:

$$-\log\phi - 0.4567\left(\frac{E_a}{RT_m}\right) = \text{constant} \qquad 3.1$$

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

3-2-3 Sample Preparation and electrical measurement

The paste 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 20~40μm 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 curied 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 JEOL-6500F scanning electron microscope (SEM).

3-3 Results and Discussion

The thermal decomposition temperatures of the pastes were easily identified using the thermo gravimetric analysis (TGA) and the subsequent Derivative thermo gravimetric analysis (DTG). **Figure 3-1** and **Figure 3-2** show the DTA and DTG results of the paste prepared from the silver flake powder and α-terpineol. The TGA results reveal ≈15% weight loss in the temperature ranging between 125°C and 180°C, and ≈0.3% weight loss between 225°C and 250°C. The derivative weight changes shown at DTG results have two maxima at 174.4°C and 241.8°C. Comparing the paste formulation indicated in **Table 3-2**, it is easily identified that the first peak corresponds to the thermal decomposition of α-terpineol, and second peak belongs to the decomposition of the lubricant coated on silver flake. The activations energies of the corresponding decompositions (E_a) calculated form DTG results are shown at Table 3-3. These results were consistent with those reported by C.P Wong et al. [6-8]. 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. It is known that common solvents, such as methanol, THF, and acetone, don't have obvious effect on the removal of silver lubricant and the thermal decomposed temperature ranges between 230 and 250°C. The results of present study show that the paste needs to be heat-treated over 230°C in order to decompose the fatty acid on silver surface. Incomplete decomposition

of the fatty acid on the surfaces silver flake will obstruct the connectivity of the silver particles and result in a higher resistivity.

Figure 3-3 shows the DTG results of the paste prepared from the silver flake powder, α-terpineol, and various MOD agents. For the silver paste with silver 2-ethylhexanoate addition, it shows that weight loss continues to increase as the paste was heated up and totally 15% weight loss was observed as the temperature reaching 200°C. Three decomposition points were exhibited at 148.0°C, 190.3°C and 257.2°C. The first peak corresponds to the decomposition temperature of α-terpineol, which is lower than that of pure silver flake paste (174.4°C). The activation energy of the decomposition was reduced to 6.79kJ/mole, which may due to the fact that 2-ethylhexanoate is a peroxide compound that may release heat to promote the decomposition of solvent [4]. The second peak at 190.3°C with decomposition activation energy 28.03 kJ/mole corresponds to the interaction between silver 2-ethylhexanoate and α-terpineol. Pure silver 2-ethylhexanoate was decomposed at 235°C. The third peak corresponds to the decomposition of the lubricant coated on silver flakes.

The DTG curve for silver paste with silver oxalate addition shows three decomposition points at 170.7°C、212.1°C and 226.4°C, corresponding to the decomposition of the α-Terpineol, the silver oxalate, and the lubricant of fatty acid, respectively. Since silver oxalate is not soluble in α-terpineol [9-10], the temperature of the solvent decomposition was not affected. The decomposition of silver oxalate at 212.14°C releases a large amount of heat and reduces the curing temperature of the silver paste.

The DTG curve for silver paste with MOD agent of silver stearate shows

the decomposition temperatures at 154.7°C, 230.1°C and 250.2°C. The solvents decomposition temperature was reduced to 154°C, similar to that for silver paste with silver 2-ethylhexanoate addition. The metal organic salts and α-terpineol have a similar polarity, so that the metal salt can be dissolved in the solvent. It changes the decomposition temperature of α-terpinol. The thermal decomposition temperatures of the silver stearates and the fatty acid on the silver flake powder surface are very close, which are approximately at 250°C, similar to that reported in the literature [11]. The silver stearate is a derivative salt from stearic acid whose structure and composition are similar to those of fatty acid [12]. So the silver stearate can easily wet the flake silver powders and distributes uniformly between the metal powders. The stearic acids are widely used as the conductive fillers in most isotropically conductive adhesives (ICA) formulations to affect the viscosity of conductive adhesive paste. The silver stearate can be interpreted in terms of three-dimensionally stacked silver caroboxylate layer with large interlayer lattice dimension. The decomposition activation energy of α-terpineol is 5.84kJ/mole, which was not influenced by the added silver stearate.

The DTG curve for silver paste with MOD agent of silver 4-cyclohexy butyrate shows three decomposition peaks at 158.9°C, 216.8°C and 254.0°C, that correspond to the decompositions of solvent, the hydrocarbons, and the fatty acid, respectively. In the molecule structure of 4-cyclohexyl butyrate, there are two kinds of carbon chain including hexahydrobenzene and CH_2-CH_2-CH_2. It is different from the silver 2-ethylhexanoate which consists of hexahydrobenzene and hydrocarbon chain. Only hydrocarbon chain exists in the silver 4-cyclohexy butyrate. The existing of hexahydrobenzene structure possesses a higher thermal

stability and thus increases the decomposition temperature.

For the MOD agent of behenic acid silver salt added, the silver paste has four decomposition temperature peaks at 140.4°C, 236.9°C, 260.0°C and 293.3°C, which correspond to the decompositions of the solvent at 140.4°C, the hydrocarbons at 236.9°C and 293.3°C, and fatty acid at 260.0°C. Behenic acid silver salt reduces the thermal decomposition temperature and activation energy (4.34kJ/mole) of the solvent. The long carbon chain of behenic acid silver salts requires high decomposition temperature (293.3°C).

Figure 3-4(a) and **Figure 3-4(b)** show the resistivity of silver films with additions of various MOD agents cured for different times at 250°C and 300°C, respectively. Generally, the resistivities of the various films reach their minimum values as the curing time longer than 10 min. For the films curing at 300°C, the minimum values were attained as long as the curing time of 5 min, except that for the film prepared form the silver paste with the addition of behenic silver salt whose decomposition temperature is at 293.3°C, as shown in **Figure 3-3**.

Figure 3-5(a) and **Figure 3-5(b)** show the resistivity of silver films with additions of various MOD agents cured at different temperatures for 5 min and 10 min, respectively. The resistivities of the films decrease as the curing temperature increases. For the curing time of 5 min (**Figure 3-4(a)**), it is evident that the resisitivity values of silver films with silver stearate, silver oxalate, and silver 2-ethylhexanoate significantly reduce down to their minimum values at temperature of 250°C. The thermal decomposition of MOD agents leads to metallic silver, CO, CO_2, the corresponding acid, and products of the organic radical reaction [11,12]. The metallic silver particles provide the linking of the

flake silver powders and thus increase the conductivity of the films. However, the silver films with cyclohexybutyrate and behenic acid silver salt additions, the minimum values won't achieve until the curing temperature reaches 300°C. Below this temperature, the MOD agents, silver cyclohexybutyrate and behenic acid silver salt, were not decomposed and existed between flake silver powders to increase the resistivity, as shown in **Figure 3-3**. Comparing the films after the decomposition of MOD agents, not all the films possess low resistivity compatible to the pure silver film, particular for films with behenic acid silver salt. After thermal decomposition of the MOD agent, it produces metallic silver and paraffin. The paraffin affects the conductivities by obstructing the channel for electric moving to reduce the silver powder continuity and led to increase the resistively [12].

At curing time of 10 min, beside the behenic acid silver salt, all the pastes with additions of MOD agent reaches their minimum values. Among the various MOD agents, the silver 2-ethylhexanoate possesses the lowest decomposition temperature (190.3°C), which forms silver particles to promote the linking of the flake silver powders and thus reduces the resistivity down to <10μΩ-cm at the temperature as low as 200°C (**Figure 3-5(b)**). Comparing the resistivities in **Figure 3-4(a)** and **Figure 3-4(b)**, curing time of 5 min was not enough time for complete decomposition of the MOD agents.

SEM micrographs of then films after curing at 250°C for 5min are shown in **Figure 3-6**. For the films prepared from pure silver paste and that with silver 2-ethylhexanoate addition show neckgrowth between silver flakes. The fatty acid coating on pure flake silver powder was decomposed near 250°C, and silver 2-ethylhexanoate thermally decomposes at 190°C and enhances the network

structure for silver metal powder. Microstructures of films prepared from other pastes do not have a significantly difference and exhibit flaky-like microstructure.

SEM micrographs of films after curing at 350°C for 30min are shown in **Figure 3-7**. Neckgrowth between the silver flakes was observed for films prepare from all the systems. All metallo-organic compounds additive were thermal decomposed and remnant metallic silver particles provide the flake silver particle to form the metal bridges. All cases show different levels of open porosities in the microstructures, especially for film prepared from the pure silver paste without addition of MOD agent, which formed very porous structure. The existence of the open porosity in the metallization is usually harmful to the plating or reliability of the devices. The benefit of the MOD agent addition is thus evident.

3-4 Summary

The metallo-organic compounds were combined with the flake silver powder for use in low curing silver paste. In this study, Among the various MOD agents, the silver 2-ethylhexanoate possesses the lowest decomposition temperature (190.3°C), which forms metallic silver particles to promote the linking of the flake silver powders and thus reduces the resistivity down to <10μΩ-cm at the temperature as low as 200°C. All cases show microstructures with different levels of open porosities, especially for film prepared from the pure silver paste without addition of MOD agent, which formed very porous structure.

References

1. V. Subramanian, Paul C. Chang, J. B. Lee, A. R. Murphy, D. R. Redinger and S. K. Volkman, “Progress Toward Development of All-Printed RFID Tags: Materials, Processes, and Devices,” Proceeding of the IEEE., 93 [7], 1330-1338 (2005).

2. K. F. Teng and R. W. Vest, “Liquid Ink Jet Printing with MOD Inks for Hybrid Microcicuits,” IEEE, Trans. Components, Hybrid, and Manufacturing, V CHMT-12 (4), 545-549 (1987).

3. P. H. Kydd, “Electrical Conductors Formed from Mixtures of Metal Powders and Metallo-organic Decomposition Compounds,” United State Patent, 6,036,889 (2000).

4. P. H. Kydd, “Low Temperature Method and Compositions for Producing Electrical Conductors,” PCT Patent, WO 98/37133 (1998).

5. C. D. Doyle, “Kinetic Analysis of Thermogravimetric Data,” J. Appl. Polym. Sci., 285 (1961).

6. D. Lu and C. P. Wong, “Thermal Decomposition of Silver Flake Lubricants,” J. Therm. Analy. Calori., 61, 3-12 (2000).

7. D. Lu, Q. K. Tong, and C. P. Wong, “A Study of Lubricants on Silver Flakes for Microelectronics Conductive Adhesives,” IEEE, Trans. Components. Packaging. Tech., 22 [3], 365-371 (1999).

8. C. P. Wong, D. Lu and Q. K. Tong, “A Fundamental Study on Silver Flakes for Conductive Adhesives,” IEEE, International Symposium on Advanced Packaging Material, 256-260 (1998).

9. V. V. Boldyrev, “Thermal Decomposition of Silver Oxalate,” Thermochimica

Acta., 388, 63-90 (2002).

10. D. Y. Naumov, E. V. Boldyreva, N. Y. Podberezskaya and J. A. K. Howard, “The Role of ‘Idel’ and ‘Real’ Crystal Structure in the Solid-State Decomposition of Silver Oxalate,” Solid. State Ionics, 101-103, 1315-1320 (1997).

11. S. J. Lee, S. W. Han, H. J. Choi and K. Kim, “Structure and Thermal Behavior of Layered Silver Carboxylate,” J. Phys. Chem. 2892-2900, 106, B 2002.

12. N. F. Uvarov, L. P. Burleva, M. B. Mizen, D. R. Whitcomb and C. Zou, “Conductivity of Long-Chain Silver Carboxylates and Their Thermal Decomposition Products.”., Solid State Ionics, 31-40, 107 (1998).

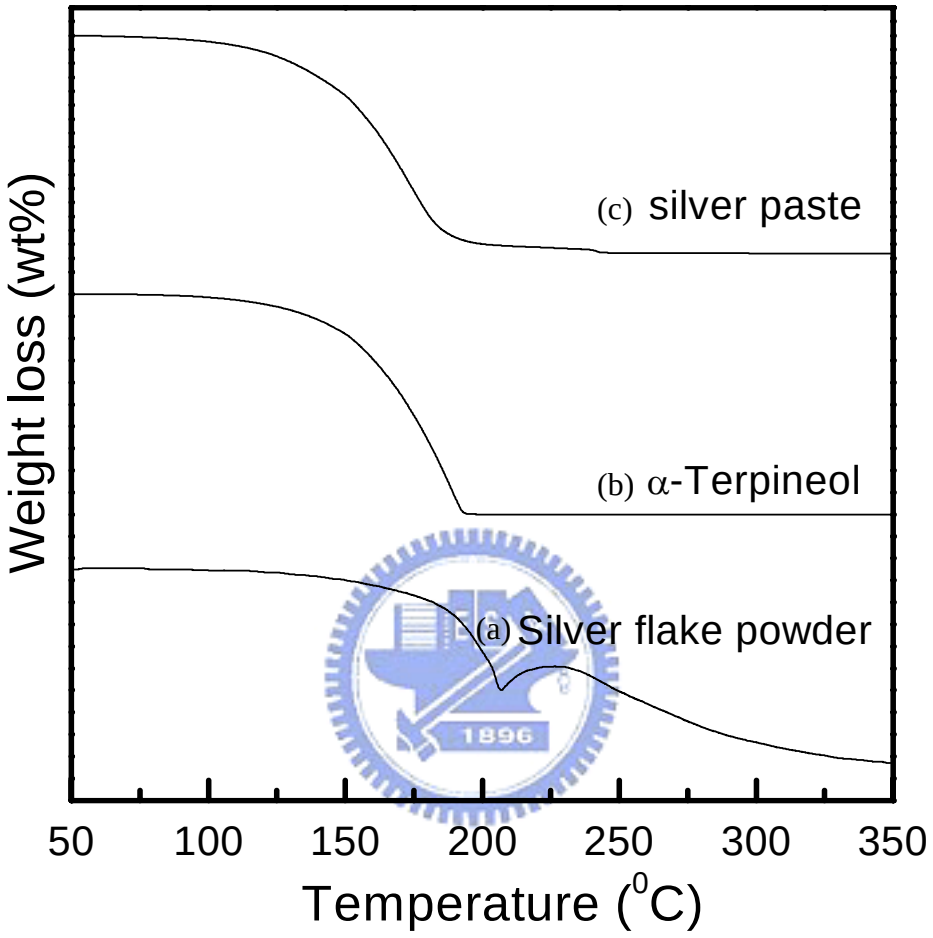


Figure 3-1. Thermo gravimetric analysis of (a) silver flake powder, (b) α-terpineol solvent, and (c) silver paste.

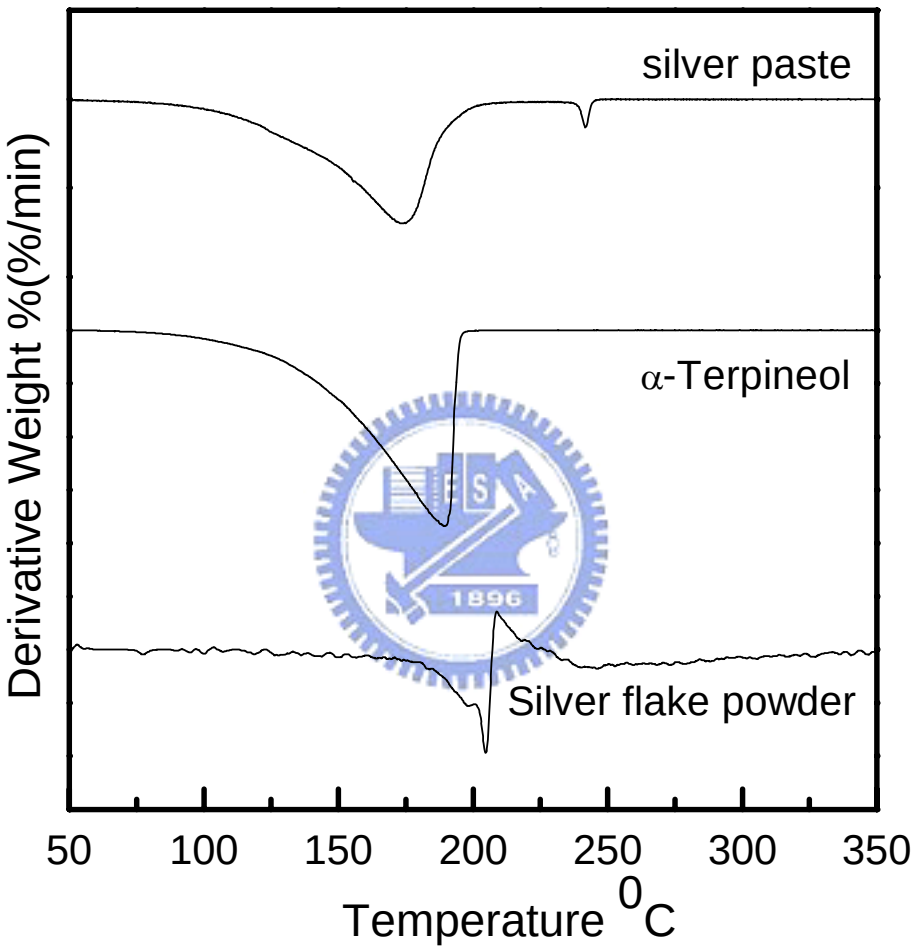


Figure 3-2. The derivative thermo gravimetric analysis of (a) silver flake powder, (b) α-terpineol solvent, and (c) silver paste.

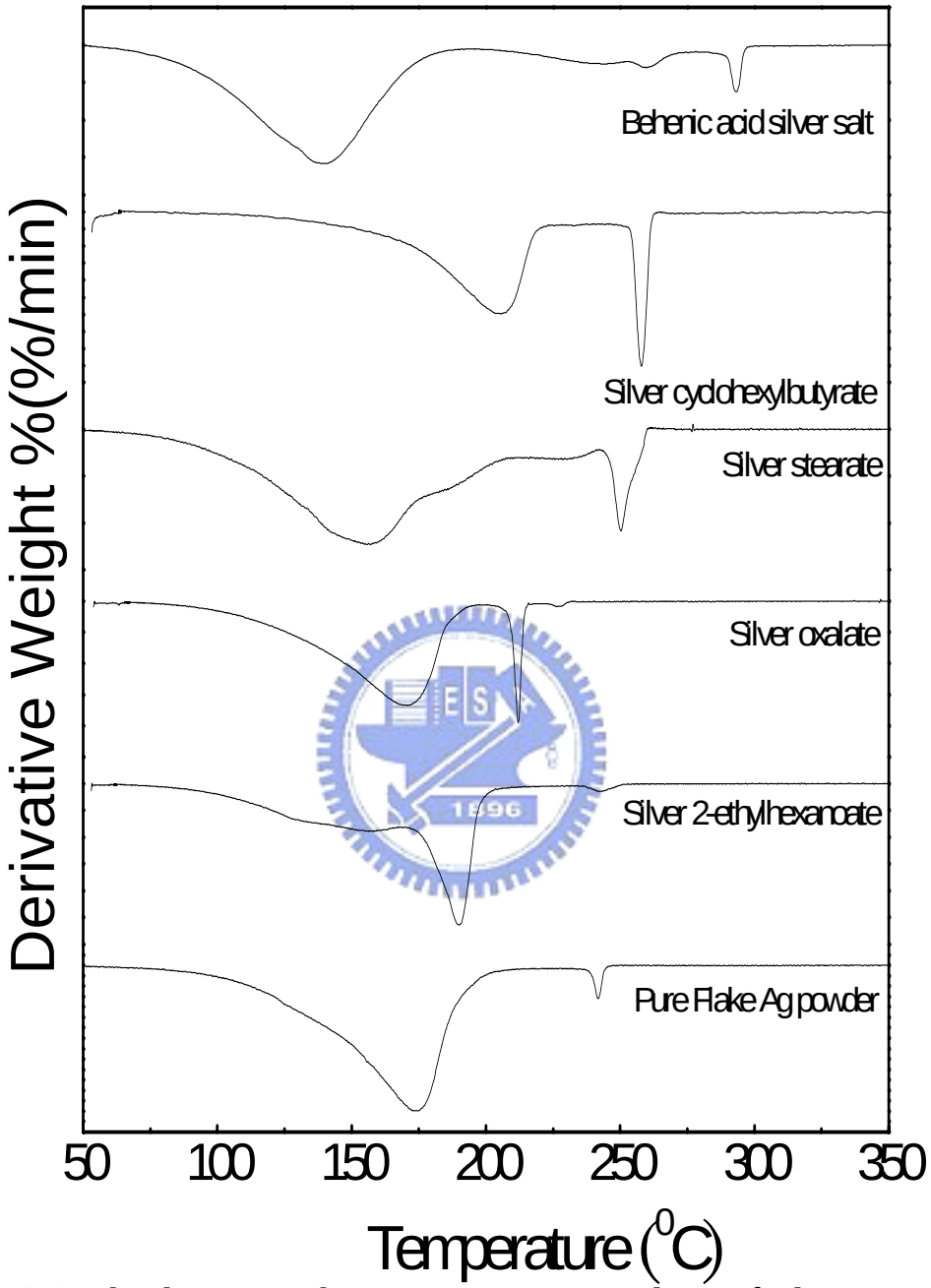


Figure 3-3. The derivative thermo gravimetric analysis of silver pastes with various MOD agents.

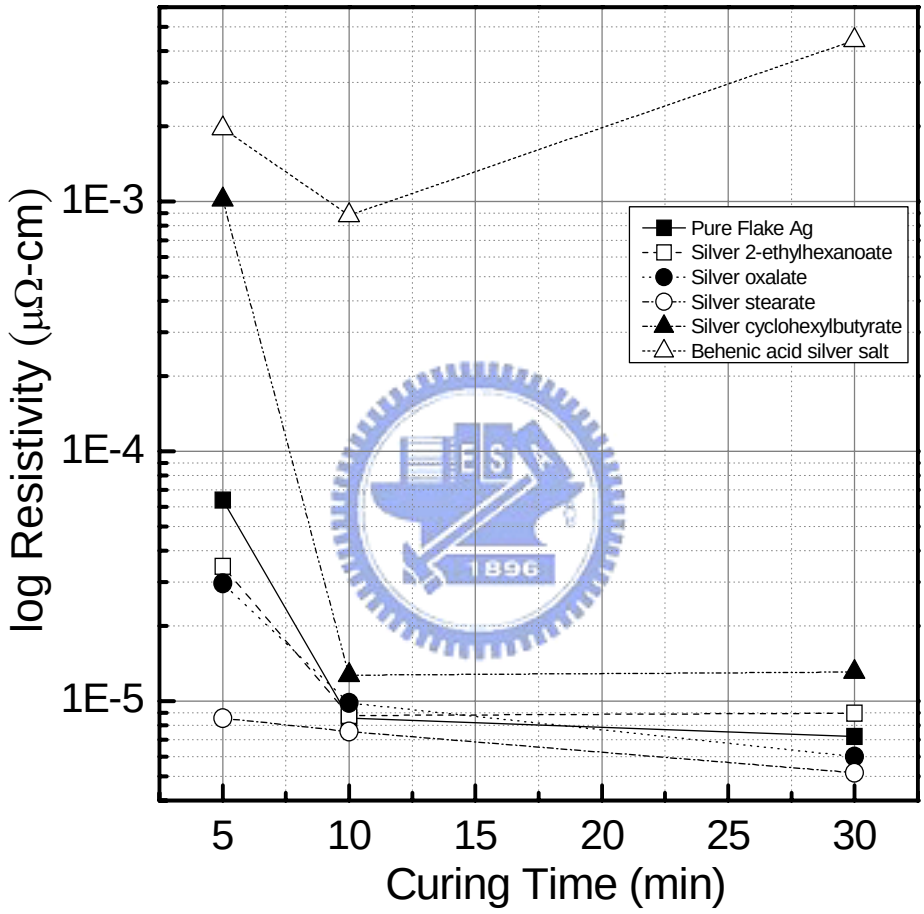


Figure 3-4(a). The resistivity of silver films with additions of various MOD agents cured for different times at 250°C.

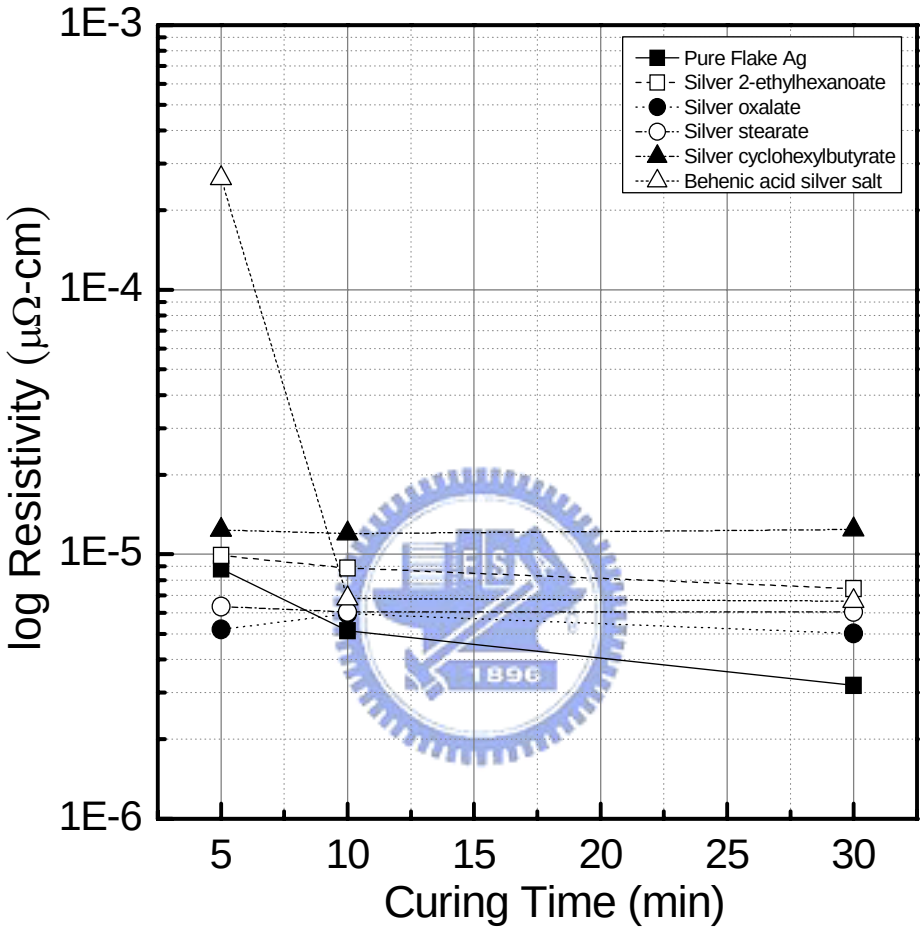


Figure 3-4(b). The resistivity of silver films with additions of various MOD agents cured for different times at 300°C.

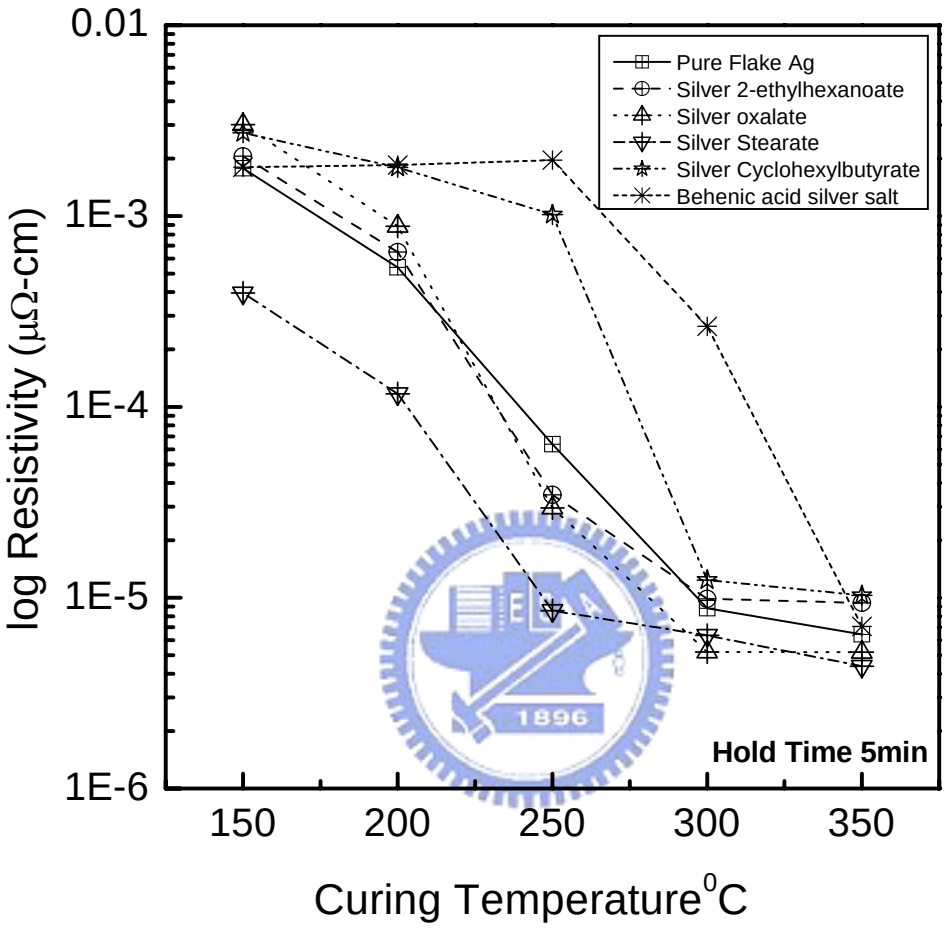


Figure 3-5(a). The resistivity of silver films with additions of various MOD agents cured at different temperatures for 5 min

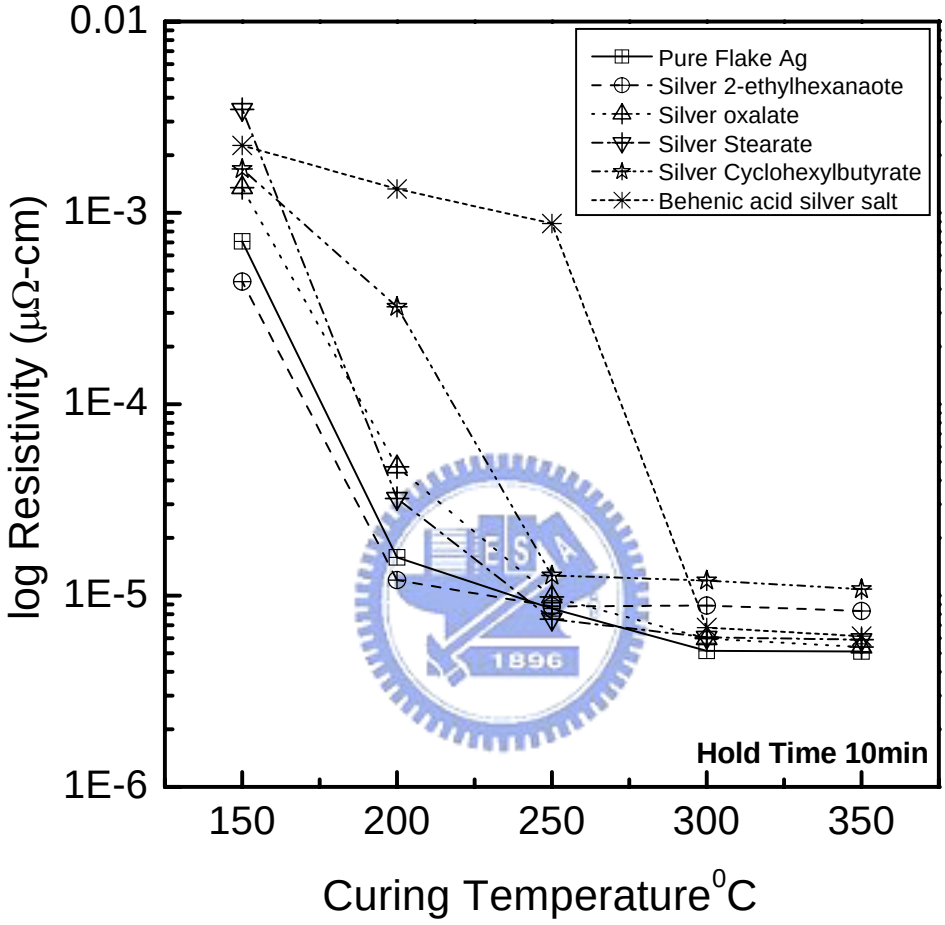


Figure 3-5(b). The resistivity of silver films with additions of various MOD agents cured at different temperatures for 10 min.

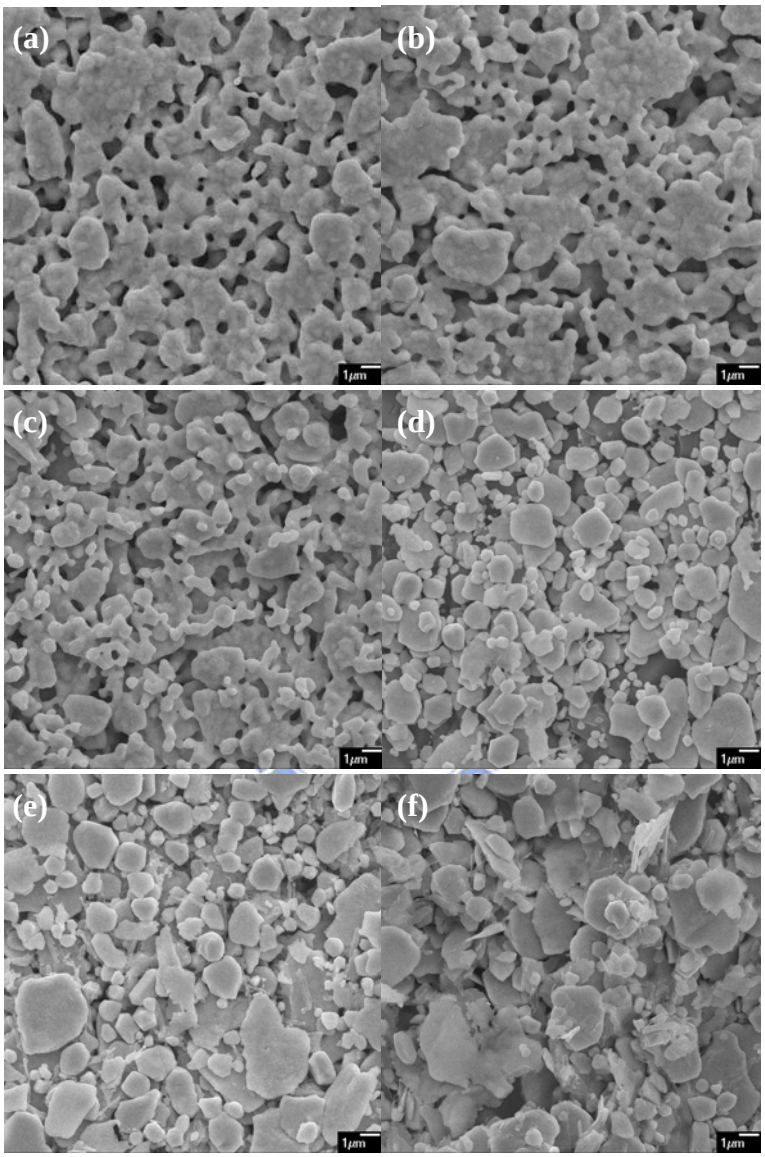


Figure 3-6. SEM micrographs of the silver films with additions of various MOD agents and cured at 250°C for 5min.

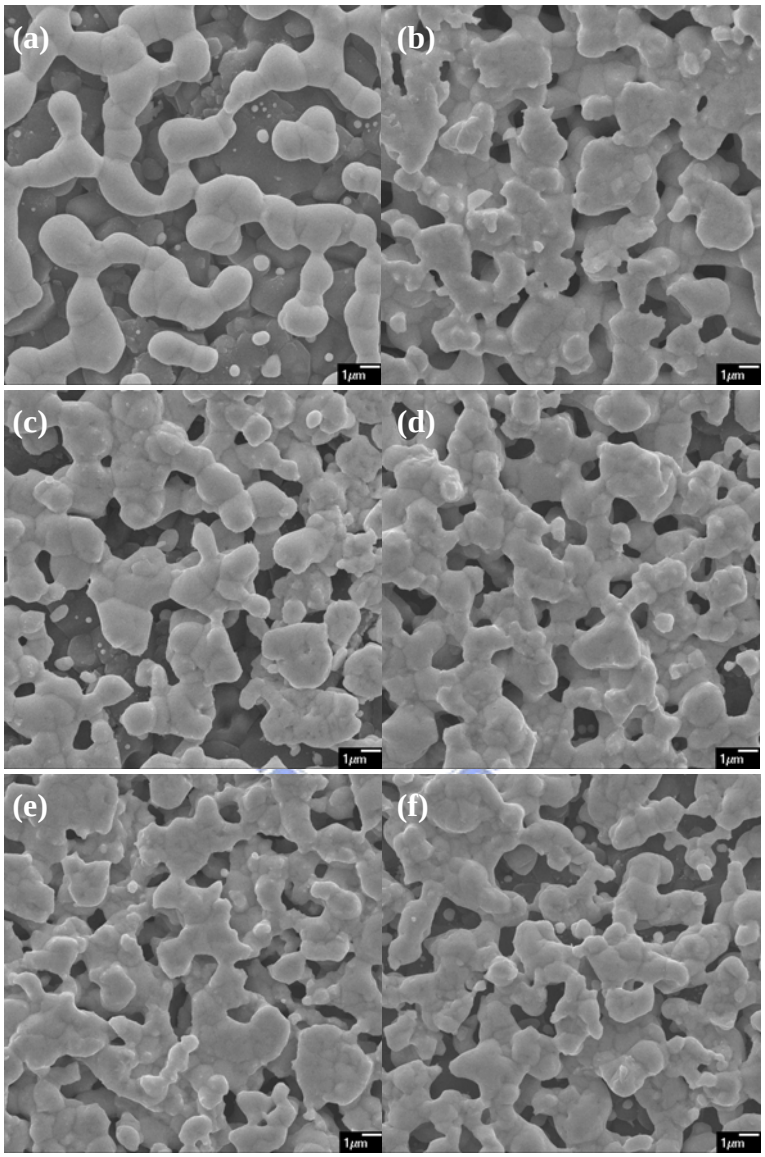


Figure 3-7. SEM micrographs of the silver films with additions of various MOD agents and cured at 350°C for 30min.

Table 3-1. Information of MOD Chemicals

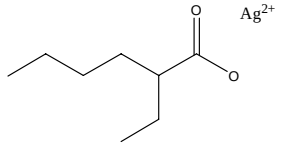
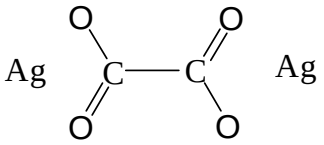
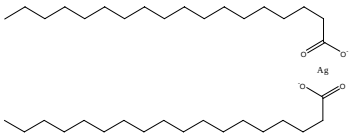
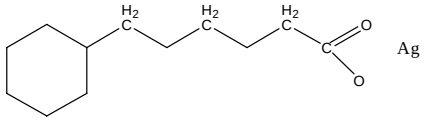
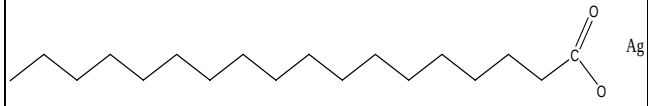
MOD Agent	Mol. W	Chemical formula	Chemical Structure
Silver 2-ethylhexanoate	$AgOOCCH(C_2H_5)C_4H_9$	251.08	
Silver Oxalate	$Ag_2C_2O_4$	303.78	
Silver Stearate	$[Ag(O_2C(CH_2)_{16}CH_3)_2$	1343.74	
Silver Cyclohexlbutyrate	$C_6H_{11}(CH_2)_3CO_2Ag$	277.11	
Behenic Acid Silver Salt	$CH_3(CH_2)_{20}COOAg$	447.44	

Table. 3-2. Formulations of the low curing pastes with various MOD additives

Formulation No.	MOD Agent		Silver Flake Powder	α-Terpineol
1	------	-----	85wt%	15wt%
2	Silver 2-ethylhexanoate	4wt%	81wt%	15wt%
3	Silver Oxalate	4wt%	81wt%	15wt%
4	Silver Stearate	4wt%	81wt%	15wt%
5	Silver Cyclohexlbutyrate	4wt%	81wt%	15wt%
6	Behenic acid silver salt	4wt%	81wt%	15wt%

Table. 3-3. Decomposition activation energies of the species in the silver pastes with various MOD additives, calculated form Doyle-Qzawa equation.

Formulation No.	MOD Agent	Activation Energy (kJ/mole°C)		
		First Peak	Second Peak	Third Peak
1	Pure Flake Ag	9.10 (174.382)		33.74 (241.753)
2	Silver 2-ethylhexanoate	6.79 (148.048)	28.03 (190.299)	24.41 (257.198)
3	Silver Oxalate	5.54 (170.702)	42.31 (212.104)	34.85 (226.433)
4	Silver Stearate	5.84 (154.226)	12.13 (230.132)	23.83 (250.197)
5	Silver Cyclohexlbutyrate	6.66 (158.920)	27.42 (216.831)	22.08 (253.985)
6	Behenic Acid Silver Salt	4.34 (140.377)	23.35 (236.870) 22.06 (260.000)	29.44 (293.298)