

Chapter 5

Effects of Silver Oxide Additions on the Electrical Resistivities and Microstructures of Low-Temperature-Curing MOD Silver Pastes

The thermal decomposition of silver paste with the addition of a metallo-organic decomposition (MOD) compound generally requires a curing time of greater than 10 min and a curing temperature greater than 250°C, which does not meet the requirement for high-speed production in flexible substrates. In this study, attempts to modify the curing conditions of MOD silver pastes through the substitutions of silver flakes with silver(I) oxide (Ag₂O) and silver(II) oxide (AgO) were performed. Differential thermal analysis (DTA), derivative thermogravimetric analysis (DTG), and X-ray diffraction (XRD) results indicated that the presence of residual silver oxide, which effectively catalyzes the evaporation of α -terpineol and the decomposition of silver 2-ethylhexanoate, decreases the curing temperature and shortens the soaking time. The reduced silver and the remaining Ag₂O enhance the connectivity and packing density of the silver flakes, and thus increase the electric conductivity of the films. For films prepared from pastes with 20 wt% Ag₂O or AgO, resistivities of 14×10^{-6} and 19×10^{-6} $\mu\Omega \cdot \text{cm}$, respectively, were successfully achieved after being cured at 200°C for 5 min.

5-1 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 [1,2]. Flexible substrates, such as polyethylene terephthalate (PET), polyimide (PI) and paper, have a common characteristic that they cannot maintain their stability at a temperature higher than $\sim 300^{\circ}\text{C}$. Low-temperature processing, high adhesion in polymer-based substrates, low-cost, high-speed manufacture, and high performance are thus requirements for any components in flexible electronics.

Conventional low-temperature, electrically conductive adhesives (ECA) have several limitations, such as relatively low electrical conductivity and unstable contact resistance. 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 precursors on various substrates, where the molecular nature of the compounds allows low-temperature conversion to the metal. Teng and Vest successfully produced an ink-jet printing system using silver neodecanoate MOD ink for hybrid microcircuits [3]. Also, patent literature has revealed further applications of MOD compounds combined with metal flake powder in thin-film metallization and termination, which are then built up using solder or by electroplating [4,5]. These techniques used silver metallo-organic compounds, such as a 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 decomposes to form a well-bonded, well-resolved conductor at a temperature compatible with polymer-based circuit-board substrates. The electrical conductivity is equal to that obtained by conventional thick-film conductors sintered at high temperatures ($>700^{\circ}\text{C}$).

A previous study [6] indicated that silver 2-ethylhexanoate ($\text{C}_8\text{H}_{15}\text{O}_2\text{Ag}$) possesses a very low decomposition temperature (190.3°C) among the MOD agents, and it forms silver particles to promote linking among silver flakes. A low-curing-temperature silver paste with 5 wt% silver 2-ethylhexanoate added possesses shear-thinning and thixotropic properties and a resistivity of $7.8 \times 10^{-6} \Omega\text{-cm}$ after being cured at 250°C , which is near the bulk resistivity of silver [7]. The thermal decomposition of silver paste with the addition of a MOD compound generally requires a curing time of greater than 10 min and a curing temperature of greater than 250°C . However, for the high-speed, reel-to-reel manufacturing of flexible substrates for RFID tag and smart-card applications, the curing time of the pastes has to be less than 5 min at temperatures of no more than 250°C , and the resultant film has to possess an electrical resistivity of less than $20 \mu\Omega\text{-cm}$ to achieve a the production speed of greater than 100 m/min [8-10]. In this study, attempts to modify the curing conditions of MOD silver pastes through the substitutions of silver flake by silver(I) oxide (Ag_2O) and silver(II) oxide (AgO) were performed. The effect of adding Ag_2O and AgO on the thermal properties, rheological behavior, and curing conditions of the MOD silver pastes were investigated. The microstructures and resistivities of screen-printed films on an alumina substrate after being thermally treated were characterized and discussed.

5-2 Experiment Procedure

5-2-1 Paste Preparation

The low-curing-temperature silver pastes used in this study were prepared from silver flakes (Ferro, U.S.A.), Ag₂O (TCI, Japan), AgO (TCI, Japan), the metallo-organic compound silver 2-ethylhexanoate (STREM, MA, U.S.A.), and the solvent α -terpineol (TCI, Japan). All materials were mixed using a high-speed mixer (Thinky Mixer) for 3 min and debubbled 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 flakes and silver 2-ethylhexanoate to solvent was fixed at 82:4:14. Also, 10 and 20 wt% of the silver flakes were substituted with Ag₂O or AgO to reduce the curing temperature and curing time while still retaining good conductivity of the resultant film. The AgO and Ag₂O powders have particle sizes (d_{50}) of 2.73 and 7.58 μm , respectively, measured by light scattering (HORIBA LA-910).

5-2-2 Thermal Decomposition Analyzed

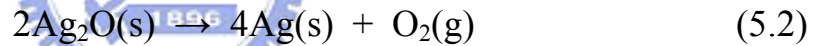
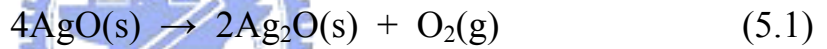
To understand the thermal behavior, thermogravimetry analysis (TGA, Perkin-Elmer) and differential thermal analysis (DTA, Perkin-Elmer 7) were performed in air at a heating rate of 10°C/min on the pastes as well as the mixtures prepared using 30 wt% silver oxides (Ag₂O or AgO) and 70 wt% α-terpineol. The derivatives of TGA traces were calculated to identify the thermal decomposition temperatures at which the mass loss is maxima. X-ray diffraction (XRD, Rigaku DMX-2200) using monochromatic Cu-Kα radiation was performed for the phase identification of the films after heat treatment.

5-2-3 Sample Preparation and electrical and microstructure measurement

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 were screen-printed on an alumina substrate for the resistivity measurement. A Keithley 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 microstructure of the films cured at various temperatures and holding times were investigated using a field-emission scanning electron microscope (SEM, JEOL-6500F, Tokyo, Japan).

5-3 Results and Discussion

The results of TGA and the subsequent derivative thermogravimetric analysis (DTG) of the α -terpineol solvent, 30 wt% Ag_2O /70 wt% α -terpineol, and 30 wt% AgO /70 wt% α -terpineol in air are shown in **Figures. 5-1(a)** and **5-1(b)**, respectively. TGA results reveal a weight loss of ≈ 72.1 wt% for 30 wt% Ag_2O /70 wt% α -terpineol and 73.9 wt% for 30 wt% AgO /70 wt% α -terpineol at temperatures ranging between 100°C and 200°C in air. Both the derivative weight changes shown in the DTG results exhibit a peak of maximum weight loss, which is associated with the decomposition of α -terpineol solvent and the reduction of the silver oxide as shown below [11,12].



The peak temperatures of the maximum weight loss for α -terpineol solvent, 30 wt% Ag_2O /70 wt% α -terpineol, and 30 wt% AgO /70 wt% α -terpineol are 188.9 , 176.8 , and 166.5°C , respectively. It appears that AgO and Ag_2O can catalyze the decomposition of the α -terpineol solvent. DTG curves shown in Fig. 1 indicate that the reaction of the AgO/α -terpineol mixture during heating occurs at a lower temperature range compared with that of $\text{Ag}_2\text{O}/\alpha$ -terpineol.

Figure 5-2 shows the DTG for the pastes without substitution and with 10 and 20 wt% Ag_2O and AgO . Reactions including solvent vaporization, reduction of the silver oxide, thermal decomposition of the MOD compound, and decomposition of the lubricant on the surfaces of silver flakes occur during

heating. For the paste without silver oxide substitution, there are three peaks in the DTG curve related to the solvent vaporization (173.4°C), MOD decomposition (201.7°C), and lubricant decomposition (~254°C) [13]. The weight loss due to the lubricant decomposition is uncertain in other DTG curves because of its small quantity. When 10 wt% of silver flake powder was substituted with Ag₂O, the peak temperature corresponding to the MOD decomposition shifts to 187.6°C, and that of the solvent vaporization and the silver oxide reduction reduces to 168.6°C. As the substitution increased to 20 wt%, the two maximum weight losses for the vaporization of solvent, the reduction of Ag₂O, and the decomposition of silver 2-ethylhexanoate, converged into a peak located at 164.7°C, which indicates that Ag₂O effectively catalyzes the organic species. For the pastes with 10 and 20 wt% AgO, the catalytic effect moves both the temperatures of peak maximum weight loss to about ≈155°C.

The rheological characteristics of the pastes with various amounts of Ag₂O and AgO are shown in **Figure 5-3**. It indicates that all pastes have a pseudoplastic flow (shear-thinning) property [**Figure 5-3(a)**]. The viscosity of the paste decreases with the substitution of AgO or Ag₂O. This is due to the fact that the silver flakes is replaced by granular silver oxide particles that allow easier particle motion under shear stress. The paste containing Ag₂O has lower viscosity than the paste containing AgO, because of the larger Ag₂O particles. **Figure 5-3(b)** indicates that all pastes possess the pseudoplastic flow (shear-thinning) property with a yield point, which is beneficial to the dimensional control in the screen-printing process.

Figures **5-4(a)** to **4(c)** show the resistivities of silver films prepared from the pastes with various amounts of Ag₂O and AgO cured at different temperatures

for 5, 10, and 30 min, respectively. Generally, the film resistivity decreases with increasing curing temperature due to the better connectivity of the metal particles associated with the decomposition of silver 2-ethylhexanoate, which coincides with the results in the previous study [7]. For the curing time of 5 min, **Figure 5-4(a)** indicates that the resistivities of the films decrease with increasing amount of AgO or Ag₂O at the curing temperature of 200°C. The difference between the films decreases and approaches a value of $\approx 10 \times 10^{-6}$ Ω-cm as the curing temperature reaches 300°C. For films prepared from pastes with 20 wt% Ag₂O or AgO, resistivities of less than 20 μΩ-cm (14×10^{-6} and 19×10^{-6} μΩ-cm, respectively) were successfully achieved after being cured at 200°C for 5 min, which meets the requirements of low-temperature and high-speed manufacturing for practical applications. As the paste is heated, silver oxide undergoes self-reduction and transforms to silver particles. The reduction of silver oxides and the thermal decomposition of silver 2-ethylhexanoate proceed with time during curing. However, the residual Ag₂O found in XRD results of the film after being cured for 5 min, as shown in **Figure 5-5**, is evidence that the reactions do not proceed to completion. DTG results for the pastes with 20 wt% Ag₂O and AgO in **Figure 5-1** show a single decomposition peak located below 200°C during heating. This suggests that the remaining Ag₂O catalyzes the evaporation of α-terpineol and the decomposition of silver 2-ethylhexanoate, which decreases the curing temperature and shortens the soaking time. The reduced silver and the remaining Ag₂O enhance the connectivity of the silver flakes, and thus increase the electric conductivity of the films. Note that Ag₂O is also a good conductor and is used as a cathode for silver oxide batteries [14,15].

Figures 5-4(b) and **5-4(c)** show that after being cured for 10 and 30 min, the films prepared from the pastes with Ag₂O and AgO possess slightly higher

resistivities compared with those without substitution at the same curing temperature, although the differences among the resistivities are very small. For the films being cured for 5 min, as indicated in **Figure 5-4(a)**, the silver oxide substitution significantly reduces the resistivities of the films; however, the distinction becomes negligible as the curing time increases to 30 min. After the MOD silver 2-ethylhexanoate was decomposed, the resulting silver particles enhance the bridging of the silver flakes, and thus reduce the resistivity of the film. As the curing time increases, the remaining Ag_2O resulting from incomplete reaction retards the further reduction in the resistivity of silver films. This may be due to the lattice mismatch and the difference in the chemical nature between Ag_2O and silver, which restricts further densification of the film.

SEM micrographs of the films, prepared from the pastes without and with 20 wt% AgO and Ag_2O , after being cured for 5 and 30 min at 200°C are shown in **Figures 5-6**. The films generally contain silver grains with a wide size distribution. After curing for 5 min at 200°C , the microstructures of the films prepared from the pastes with AgO and Ag_2O contain smaller silver particles [**Figures 5-6(b)** and **5-6(c)**] than the film without substitution [**Figure 5-6(a)**]. The small silver particles fill the cavities among silver flakes and increase the connectivity of the films, and thus reduce the resistivities of the films. Prolonging the curing time, the reduction of oxides and the decomposition of silver 2-ethylhexanoate allows the completion (**Figure 5-1**) and neckgrowth between the particles is evident [**Figure 5-6(d)** and **5-6(f)**]. There is no distinct difference among the microstructures of the films prepared from the pastes without or with the oxide substitution.

5-4 Summary

In this study, MOD silver pastes with silver flakes substituted by Ag_2O and AgO to modify the curing conditions while retaining good electrical conductivity were analyzed. Results indicate that the silver oxides effectively catalyze the organic species. For films prepared from pastes with 20 wt% Ag_2O or AgO , a resistivity less than $20 \mu\Omega\text{-cm}$ was successfully achieved after curing at 200°C for 5 min, which meets the requirements of low-temperature and high-speed manufacturing of flexible substrates. The reduced silver and the remaining Ag_2O enhance the connectivity of the silver flake and thus increase the electric conductivity of the films.



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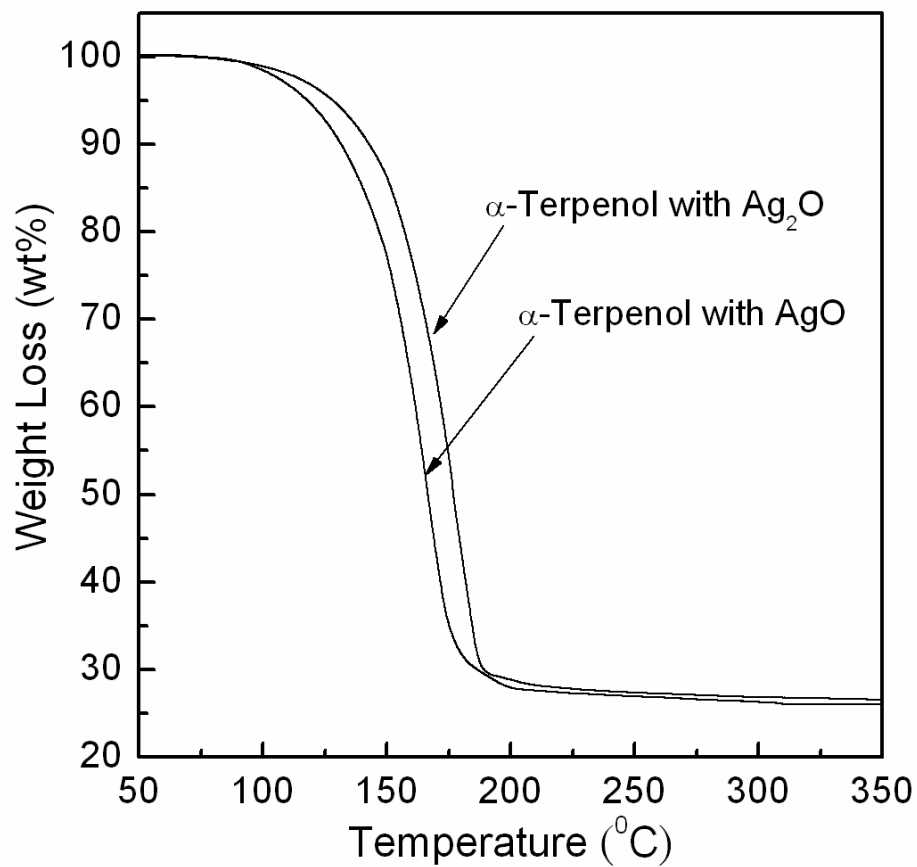


Figure 5-1(a). TGA curves for mixtures of silver oxide (Ag_2O or AgO) and α -terpenol.

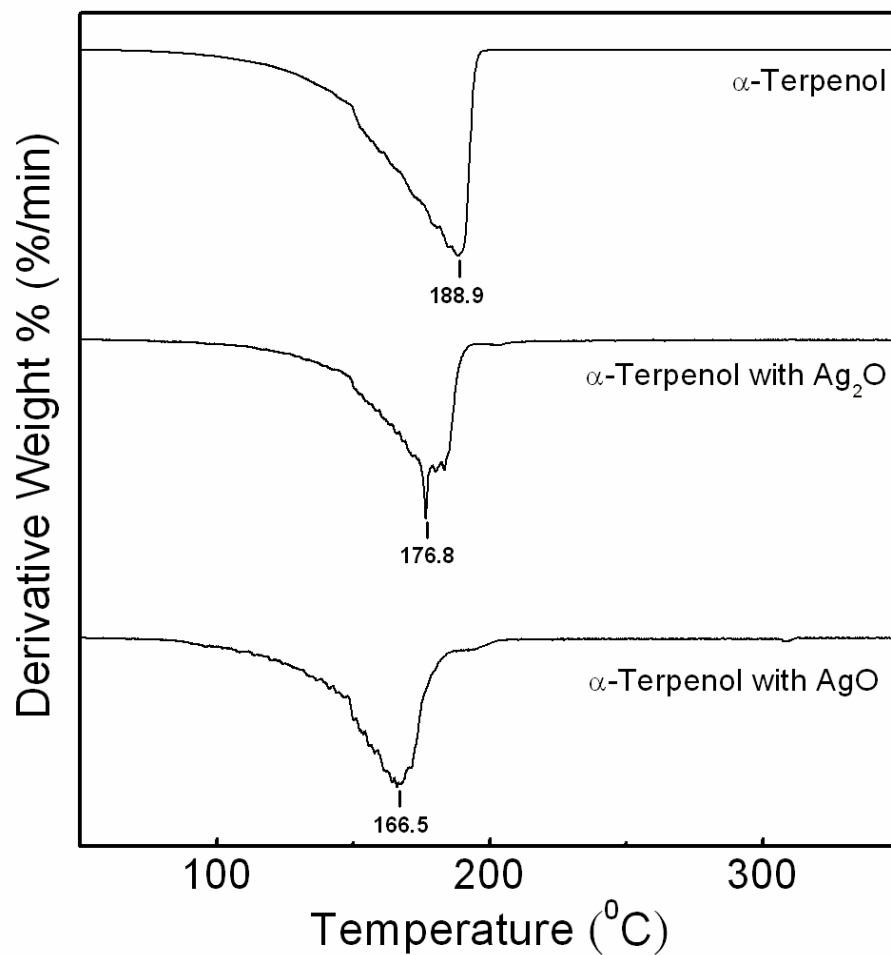


Figure 5-1(b). TGA curves for mixtures of silver oxide (Ag_2O or AgO) and α -terpenol.

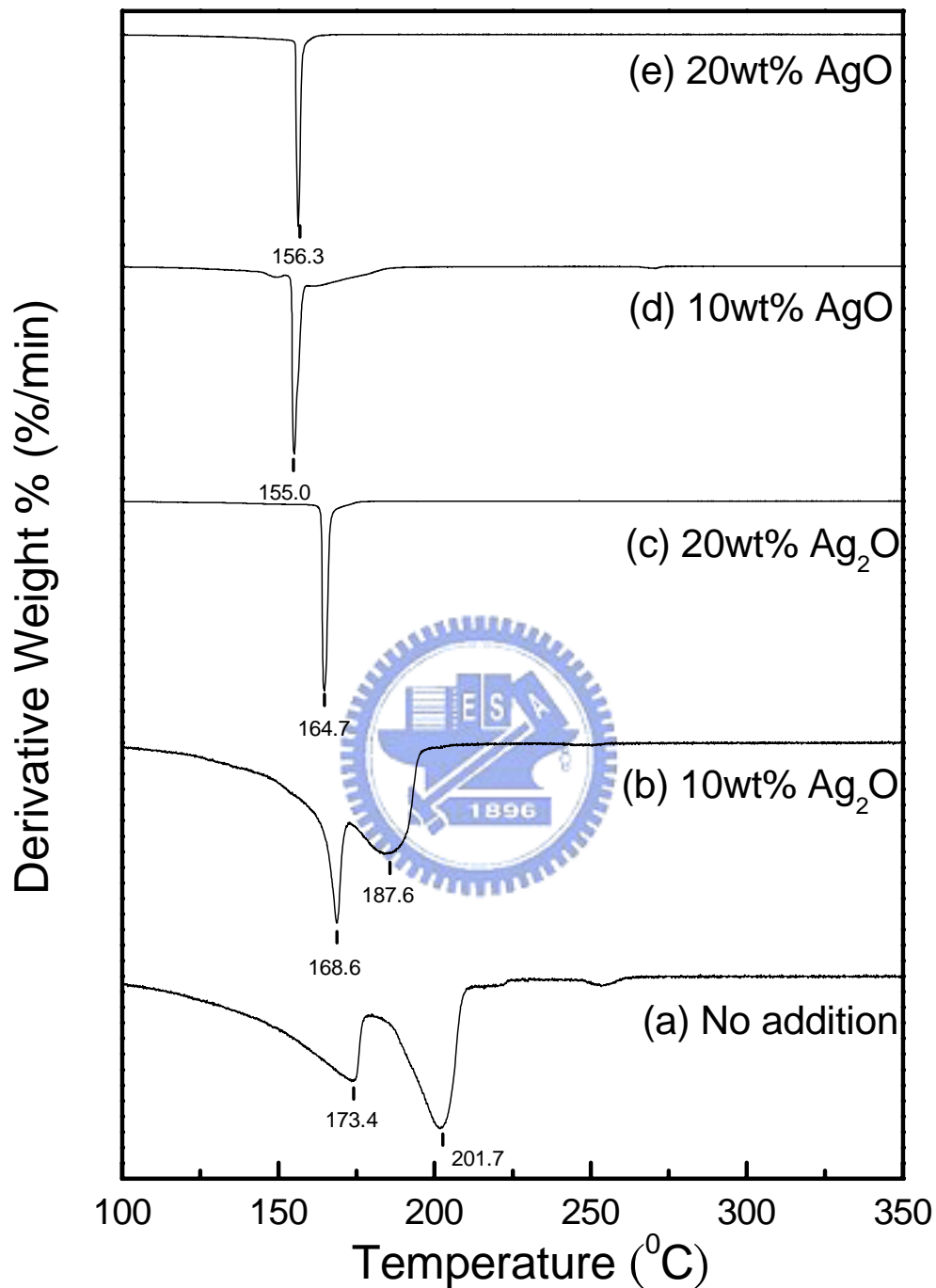


Figure 5-2. DTG curves of the (a) original silver paste, (b) paste with 10wt% Ag₂O substitution, (c) paste with 20wt% Ag₂O substitution, (d) paste with 10wt% AgO substitution, and (e) paste with 20wt% AgO substitution

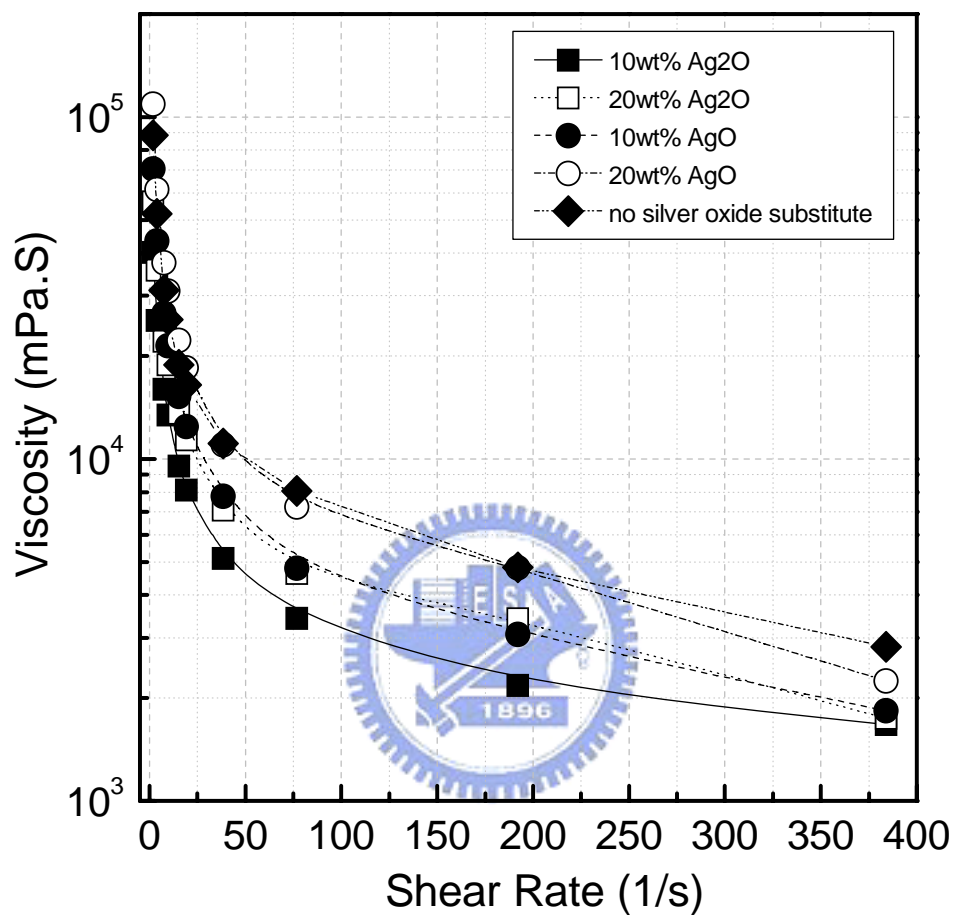


Figure 5-3(a). (a) Viscosity properties and (b) thixotropic properties of the pastes without and with silver oxide (Ag₂O or AgO) substitutions.

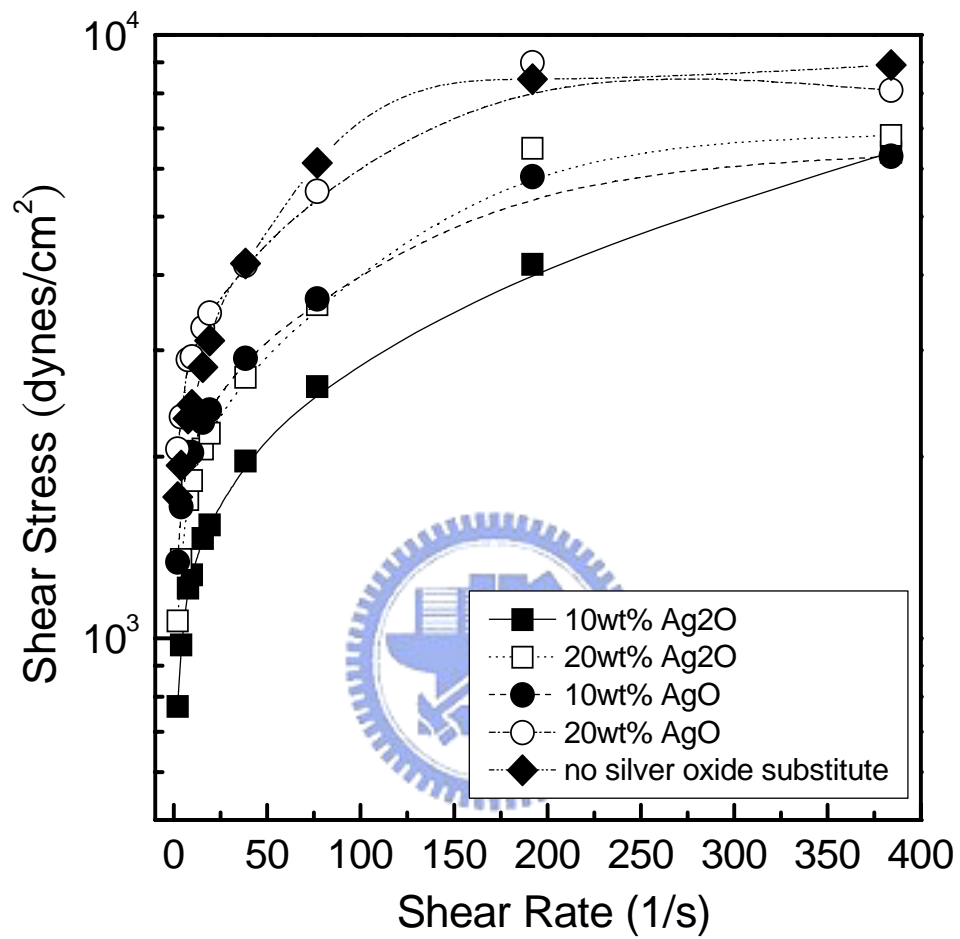


Figure 5-3(b). (a) Viscosity properties and (b) thixotropic properties of the pastes without and with silver oxide (Ag_2O or AgO) substitutions.

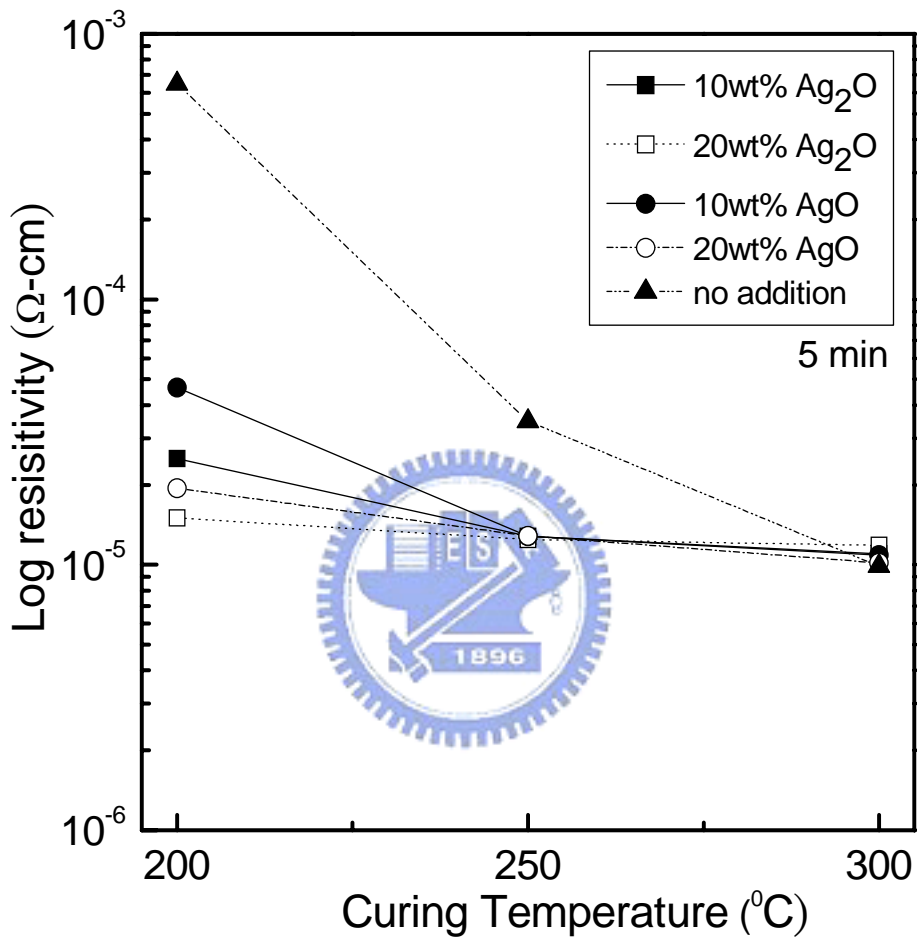


Figure 5-4(a). Resistivities of silver films prepared from the pastes without and with silver oxide (Ag₂O or AgO) substitutions and cured at various temperatures for a soaking time of (a) 5 min, (b) 10 min, and (c) 30 min.

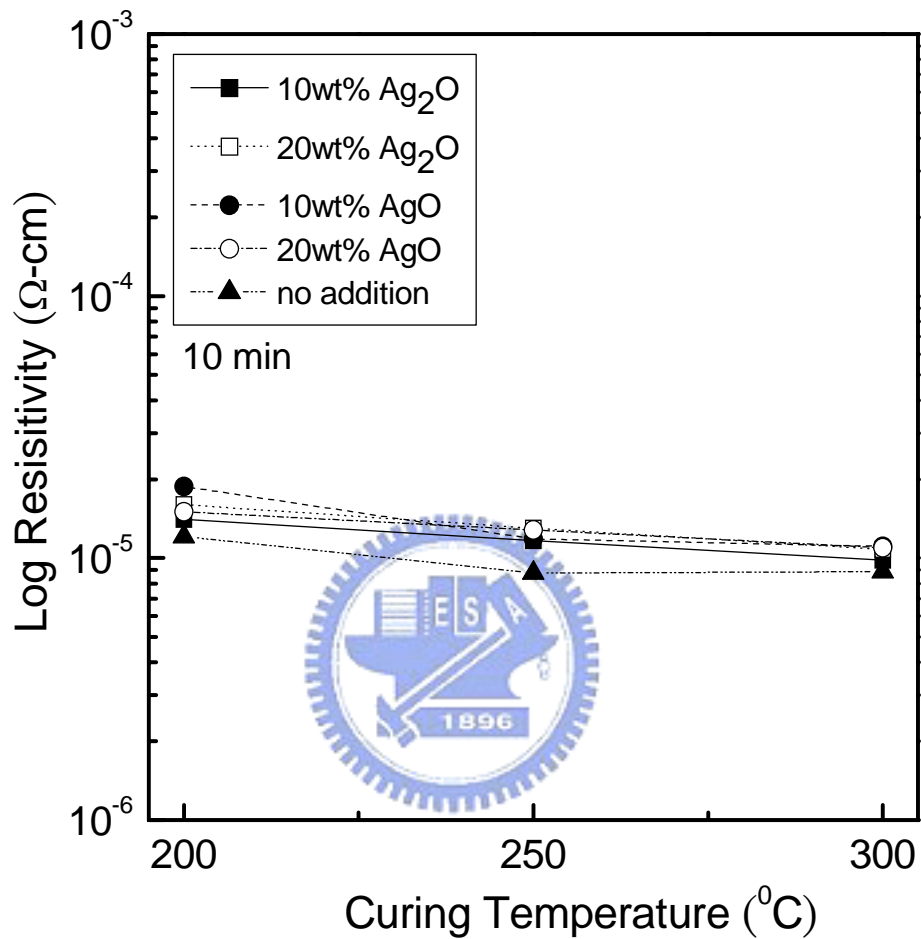


Figure 5-4(b). Resistivities of silver films prepared from the pastes without and with silver oxide (Ag₂O or AgO) substitutions and cured at various temperatures for a soaking time of (a) 5 min, (b) 10 min, and (c) 30 min.

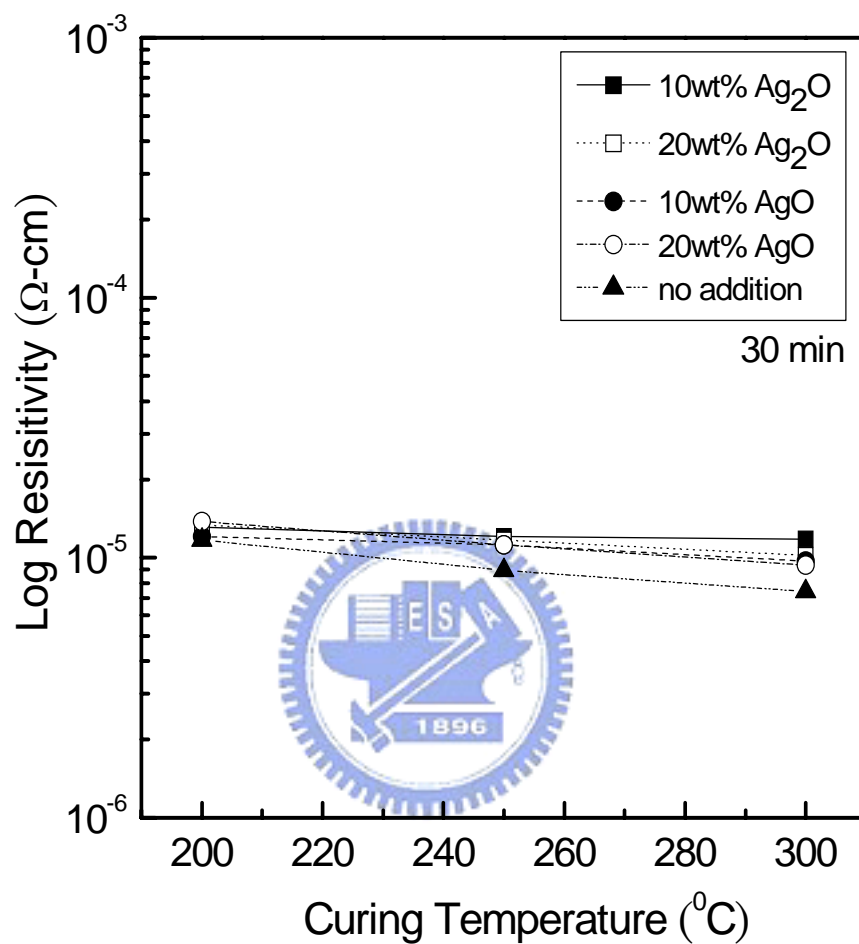


Figure 5-4(c). Resistivities of silver films prepared from the pastes without and with silver oxide (Ag₂O or AgO) substitutions and cured at various temperatures for a soaking time of (a) 5 min, (b) 10 min, and (c) 30 min.

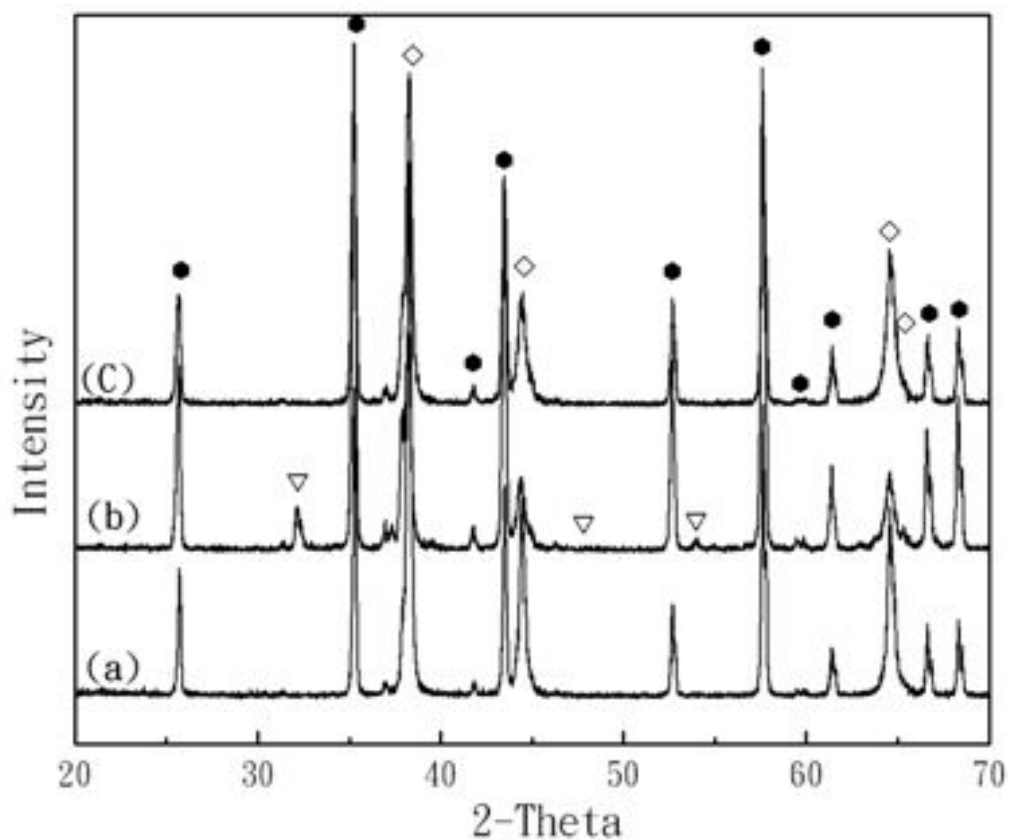


Figure 5-5. XRD patterns of (a) pure silver paste cured at 200°C for 5 min ; (b) paste with 20wt% AgO substitution cured at 200°C for 5 min; and (c) paste with 20wt% AgO substitution cured at 200°C for 30 min. (● substrate Al₂O₃; ▽ Ag₂O; ◇ Ag)

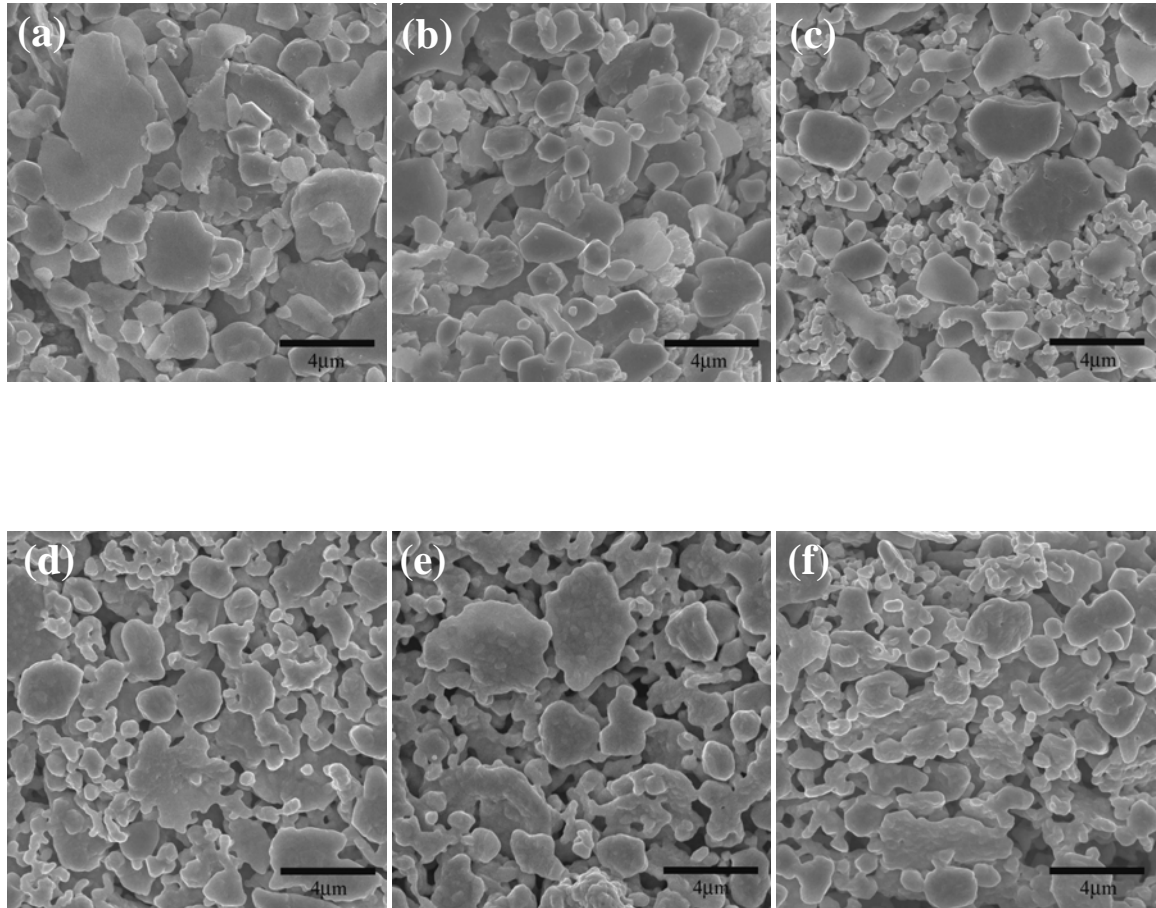


Figure 5-6. SEM micrographs of the silver films prepared from (a) original silver paste cured at 200°C for 5 min, (b) paste with 20 wt% Ag₂O substitution cured at 200°C for 5 min, (c) paste with 20 wt% AgO substitution cured at 200°C for 5min, (d) original silver paste cured at 200°C for 30 min, (e) paste with 20 wt% Ag₂O substitution cured at 200°C for 30 min, and (f) paste with 20 wt% AgO substitution cured at 200°C for 30min.