

Fabrication of Photoimageable Silver Paste for Low-Temperature Cofiring Using Acrylic Binder Polymers and Photosensitive Materials

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Abstract: Thick-film photolithography is a new technology that combines lithography processes, such as exposure and development, with the conventional thick-film process applied to screen-printing. In this study, we developed a low-temperature cofireable silver paste applicable for thick-film processing to form fine lines using photolithographic technologies. The optimum paste composition for forming fine lines was investigated. The effect of processing parameters, such as the exposing dose, had on the fine-line resolution was also investigated. As the result, we found that the type of polymer and monomer, the silver powder loading, and the amount of photoinitiator were the main factors affecting the resolution of the fine lines. The developed photoimageable silver paste was printed on a low-temperature cofireable green sheet, dried, exposed, developed in an aqueous process, laminated, and then fired. Our results demonstrate that thick-film fine lines having widths $< 20 \mu\text{m}$ can be obtained after cofiring.

Keywords: photoimageable, silver paste, low-temperature cofiring, thick-film photolithography, fine-line resolution.

Introduction

In recent days, the amount of transmitted data is increasing in wireless communication systems as the application frequency range is extended to higher frequency. In addition, for the miniaturization, the light weight, the minimum parasitic values, the increased reliability and the improved noise figure of the final product, a next generation packaging technology such as SOP (system-on-package), which enables the embedment of passive components into dielectric layers, is being paid attention to.¹⁻³ As one of the various substrate materials for this technology, LTCC (low temperature cofired ceramic) has several useful merits; low dielectric loss can be obtained compared to organic substrates, the embedment of passive elements is possible, and highly conductive metals such as silver, gold, and copper, can be used as inner conductors due to the firing temperature below $1,000^\circ\text{C}$.^{4,7}

LTCC modules are fabricated by casting green sheets with LTCC powder, punching via-holes in a green sheet, printing circuit patterns on a punched green sheet, laminating each layer to one body, and finally cofiring. However, because the general screen-printing process has limits regarding the

line resolution of thick-film circuit, the thick-film photolithography process using photosensitive paste is being researched as an alternative for fine-line patterning.⁸⁻¹⁰ Thick-film photolithography is a combined technology of thick-film process and thin-film process in that a thick-film circuit is formed by UV exposure¹¹⁻¹⁷ and development processes. A photoimageable paste is applied on a substrate and exposed to UV through photo-mask. And then, by eliminating the uncured area using aqueous solution in developer and finally firing in furnace, the thick-film fine-lines are fabricated on a substrate. Figure 1 is a schematic diagram of the procedure of thick-film photolithography process.¹⁸

In this research, several compositions of photoimageable silver paste cofireable with LTCC were fabricated using acrylic binder polymers and several photosensitive organic materials, developed on LTCC green sheet and characterized. The resolution of fine-line of each paste composition was compared to determine the optimum paste composition for fabricating fine lines.

Experimental

Materials. For fabricating photoimageable Ag paste, three types of acrylic binder polymers (KB-2, 4, and 5) and three types of acrylate monomers (M300, 310, and 340)

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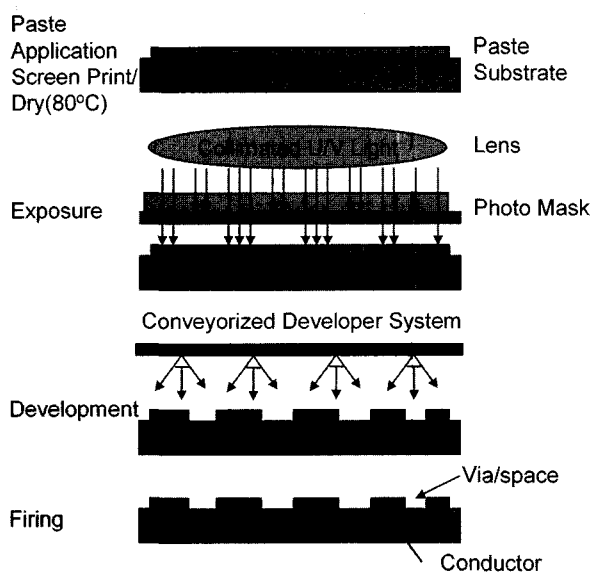


Figure 1. Schematic diagram of thick-film photolithography.

were supplied by Miwon Commercial Co. and were used as received. A photoinitiator (TPO) was also obtained from Miwon Commercial Co. Silver powders ($D_{50} = 1 \mu\text{m}$, SP3000-1) were purchased from Degussa, a dispersant (Hypermer PS-2) was purchased from Uniqema, and oleic acid as lubricant was purchased from Samchun Pure Chemical Co., respectively. Additional solvent was made by mixing α -terpineol obtained from Acros Organics with butyl carbitol acetate obtained from Samchun Pure Chemical Co. by weight ratio of 2 : 1.

Acrylic binder polymers used in this experiment have carboxylic groups (-COOH) as shown in Figure 2 so that it allows the formation of salt in the development process. In general, the development solution is made by dissolving 0.4 ~ 1.0% Na_2CO_3 in distilled water. When it is sprayed on to the dried paste surface, it reacts with the acid of binder polymer and makes the salt as shown in eq. (1). Because this salt dissolves well in water, the unexposed area of the paste is eliminated from the substrate.¹⁹ Properties of the acrylic binder polymers provided from manufacturer are summarized in Table I and their TGA graphs are shown in Figure 3.



Preparation of Photosensitive Paste and Evaluation Pattern. In order to obtain the optimum composition of

Table I. General Properties of Acrylic Binder Polymers

Sample	Viscosity (cps at 25 °C)	Acid Value (mgKOH/g)	Non-volatile Content (%)	T_g (°C)	M_n	M_w	M_w/M_n
KB-2	55,000	55.2	45.0	82.9	11,553	21,425	1.9
KB-4	47,000	49.7	40.0	94.5	16,691	28,657	1.7
KB-5	18,000	42.4	45.0	97.0	14,885	26,682	1.8

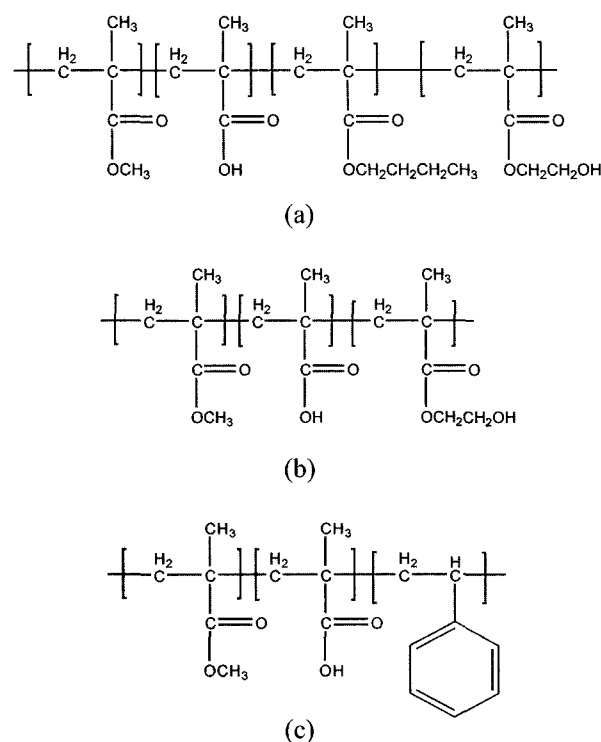


Figure 2. Structures of acrylic binder polymers: (a) KB-2, (b) KB-4, and (c) KB-5.

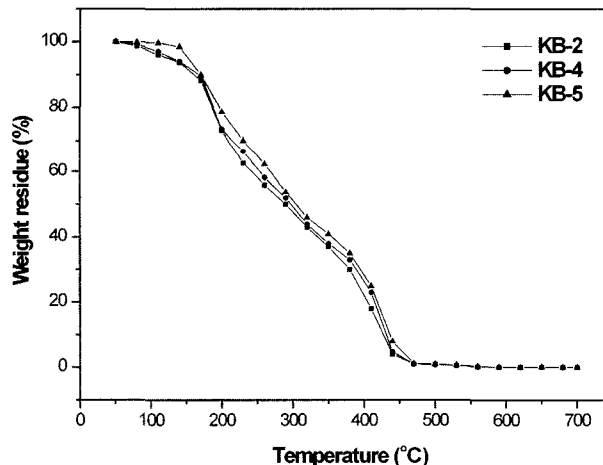


Figure 3. TGA curves of acrylic binder polymers.

photoimageable silver paste, experiments were conducted by adjusting the types and amounts of acrylic binder polymers, monomers, and photoinitiators.

Figure 4 shows the fabrication procedure of the photoimageable silver paste. The organic vehicle was made by pouring an acrylic binder polymer, a monomer, and photoinitiator into a 40 g plastic jar and mixing them for 3 min using high-speed paste mixer (Thinky, AR-250). And then, silver powders and dispersant were mixed with the vehicle. The mixture was milled for 20 min using a three-roll mill (Exact 50) in order to eliminate agglomerates in the paste, and additional solvent was added to control the viscosity of the paste. Viscosities measured by Brookfield DV-III viscometer were in the range from 60,000 to 80,000 cps after three-roll milling. Finally, the fabricated silver paste was thoroughly mixed again and defoamed for 2 min in the high-speed mixer.

After cutting a LTCC green sheet with thickness of 100 μm into the size of 100 \times 100 mm, the fabricated silver paste was printed on it using a screen mask (400 mesh, 5 μm emulsion) with 50 \times 50 mm blank pattern. After leveling for 10 min at RT, the printed paste was dried for 10 min in a convection oven at 80 $^{\circ}\text{C}$. Using KP-1200 mask aligner made by Opto Finetech, the dried paste was exposed to high dose UV of 1,500 mJ/cm^2 . Only in case of the monomer test, the exposure was conducted with 300 mJ/cm^2 step in the range from 300 to 1,500 mJ/cm^2 . The exposed paste was developed in a conveyor-type spray developer made by NTI using aqueous solution with 1 wt% Na_2CO_3 (Samchun Pure Chemical Co.) at 30 $^{\circ}\text{C}$. Developing time was in the range of 1.0 to 1.2 times TTC (time to clear) which is the time required to remove the dried unexposed paste from the substrate completely in the developer. Figure 5 shows the test pattern for evaluation of fine-line resolution, which is composed of several via patterns, wedge-type patterns and parallel line/space patterns. After development, the patterned green sheet was dried for 20 min at 80 $^{\circ}\text{C}$ in a convection oven, and then laminated on 7 dummy sheets to adjust

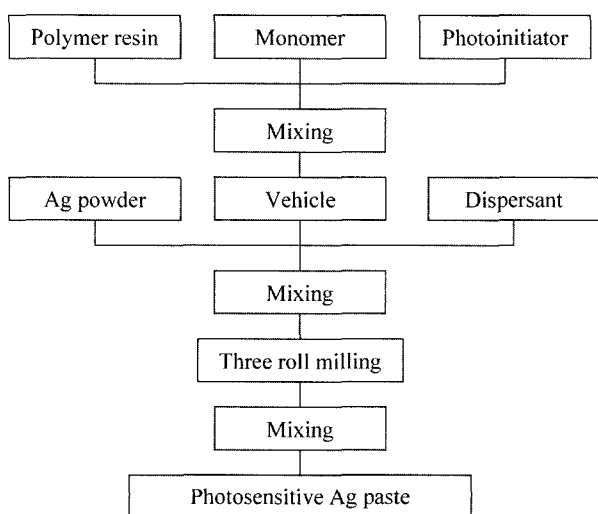


Figure 4. Fabrication procedure of the photosensitive Ag paste.

the final substrate thickness. Cofiring was conducted in belt furnace using the profile with the holding time of 25 min at the peak temperature of 850 $^{\circ}\text{C}$.

Measurement of Evaluation Pattern. Photographs of line and space patterns were taken using Camscope of Sometech and Perfection 1200U scanner of Epson and then compared according to each compositional parameter. The widths of line and space were measured before and after cofiring with Nikon measuring microscope, MM-40.

Results and Discussion

Effect of the Type of Acrylic Binder Polymer. Photolithographic properties according to three types of acrylic binder polymers were examined. Ag powder loading was fixed to 70 wt%, binder polymer to monomer ratio was 4:1, M310 was used as monomer, and the amount of photoinitiator was 30 wt% of monomer. Figure 6 shows the results of the developed patterns according to KB-2 and 4. KB-2 enabled 20 μm line and space patterns to be developed, but 20 μm line and space patterns, in case of KB-4, were damaged after development, and the paste residues were left in the space between the lines so that the unexposed area could not be clearly eliminated from the surface of green sheet. In case of KB-5, no visible pattern was developed.

2-Hydroxyethyl methacrylate (HEMA), one of the constituents of copolymer in KB-2 and 4, has -OH group which has the role of improving adhesion of paste to substrate.²⁰ The difference of the additional amount of HEMA in KB-2 and 4 resulted in the difference of the number of -OH group, and the experimental results are shown in Figure 6. It was estimated that KB-4 had too many -OH groups so that the adhesion between dried paste and green sheet was too strong, and as the result, the line resolution of the developed test pattern was degraded.

In case of KB-2, n-butyl methacrylate (nBMA), another constituent of copolymer, has a glass transition temperature ($\sim 20^{\circ}\text{C}$) much lower than that of MMA (105 $^{\circ}\text{C}$) or MAA (185 $^{\circ}\text{C}$). So, it may had the effect of softening the dried paste layer and facilitated the line resolution which improved up to 20 μm width pattern.

Because KB-5 had styrene, the glass transition temperature of copolymer was higher than that of KB-2 or 4 as shown in

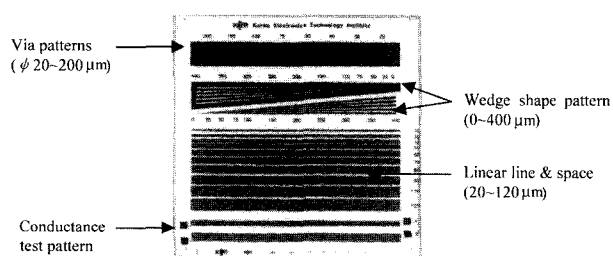


Figure 5. Test pattern for the evaluation of fine-line resolution.

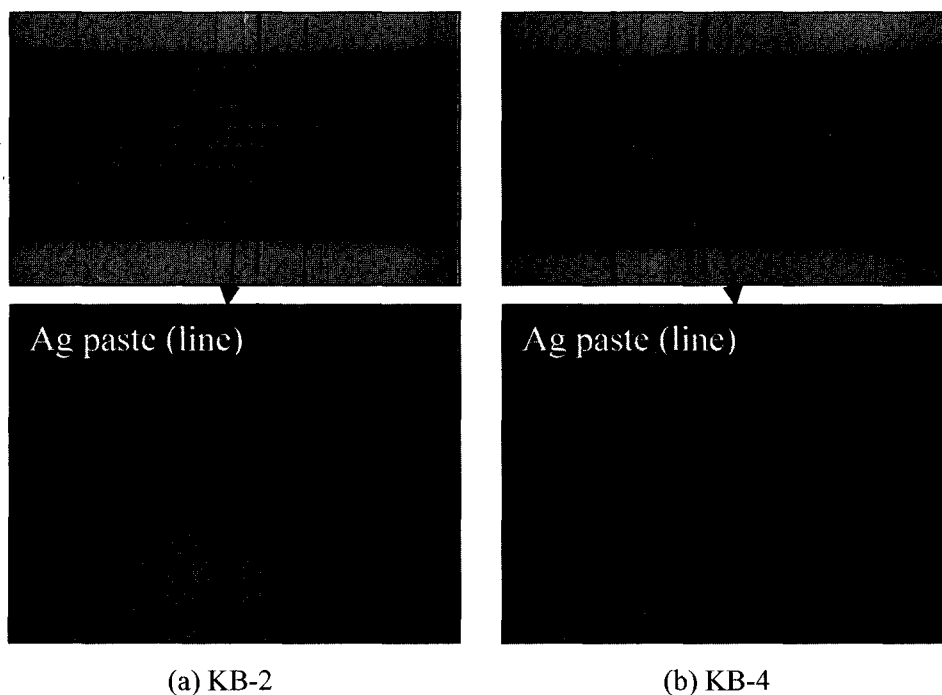


Figure 6. Comparison of 30 μm line and space patterns of KB-2 and KB-4.

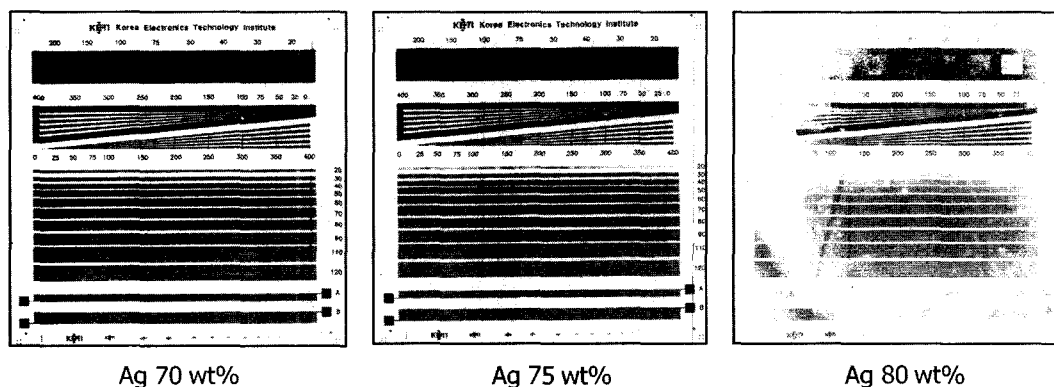


Figure 7. Comparison of test patterns after development according to silver content.

Table I so that it may have hardened the dried paste layer. Moreover, due to the relatively low acid value, the expected fine-line pattern could not be obtained.

Effect of Ag Powder Loading in Paste. Figure 7 shows the test patterns after development according to the Ag powder loadings in paste composition. The test pattern of 70 wt% loaded composition was clearly developed up to 20 μm line/space pattern. In case of 75 wt% loading, most pattern was formed, but 20 μm line/space pattern was damaged. The test pattern of 80 wt% loaded composition was mostly washed off the surface of the green sheet.

The formability of the cured area by UV exposure is dependent upon the monomer and the photoinitiator. When the dried paste was exposed to UV, photoinitiator was excited and it changed to free radical, and then, this free rad-

ical reacts with the carbon double bonding of the monomer and instantaneously makes the photo-polymerized chains. These polymer chains harden the exposed area, so this area has low solubility in development solution and remains as the circuit pattern after development.¹⁹ In case of higher powder loading, the relative amounts of monomer and photoinitiator decreased, and the hardening degree of exposed area also reduced so that the fine-line patterns were damaged by the developing solution. As a result, the lower the Ag powder loading, the higher line resolution was obtained.

In addition, as one of the important factors determining the powder loading, the shrinkage matching between paste and green sheet must be considered.²¹ Shrinkage matching test patterns were made by printing 20 \times 20 mm square patterns on green sheet, laminating with 2 dummy layers, cut-

Table II. Compositions and Chemical Structures of Monomers

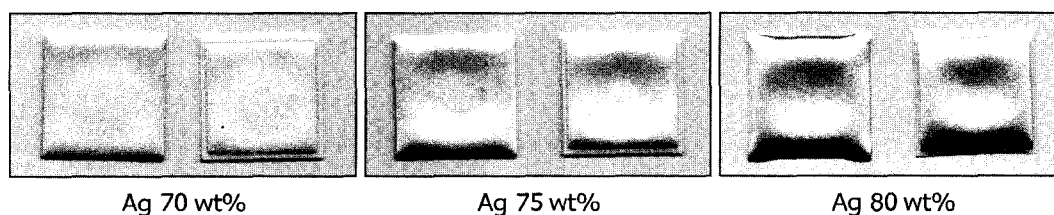
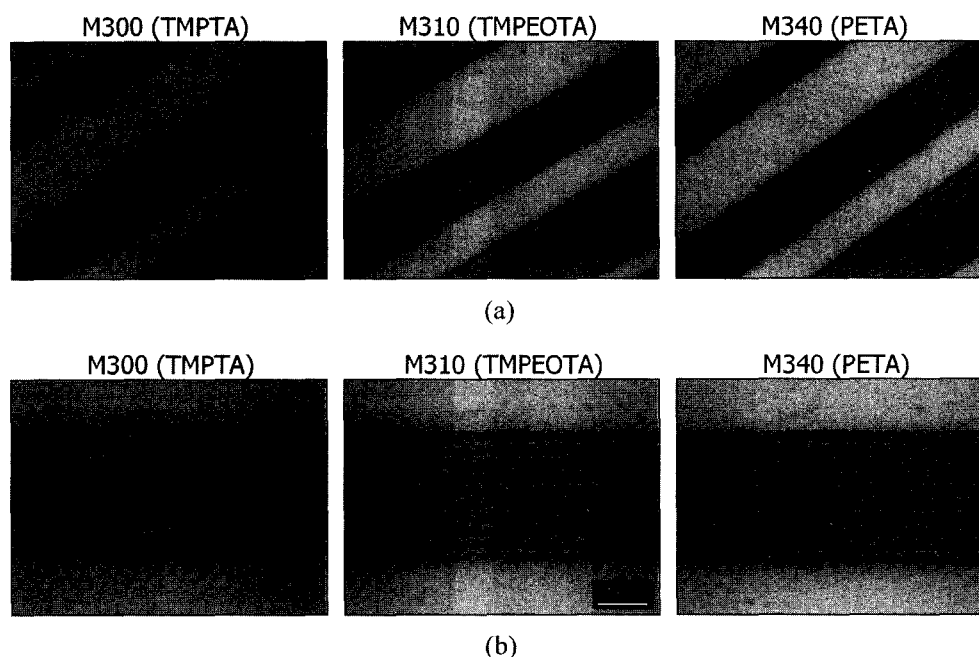
Code	Compositions	Chemical Structure
M300	Trimethylolpropane Triacrylate (TMPTA)	$(\text{CH}_2=\text{CHCOOCH}_2)_3\text{C}-\text{CH}_2\text{CH}_3$
M310	Trimethylolpropane Ethoxylated Triacrylate(TMPEOTA)	$[\text{CH}_2=\text{CHCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2]_3\text{C}-\text{CH}_2\text{CH}_3, n \approx 3$
M340	Pentaerythritol Triacrylate (PETA) mixed with Pentaerythritol Tetraacrylate (PETTA)	$(\text{CH}_2=\text{CHCOOCH}_2)_3\text{C}-\text{CH}_2\text{OH}$

ting the laminate to the test size, and then cofiring. Figure 8 shows the result of shrinkage matching test. Composition with 70 wt% Ag powder loading generated relatively better matching results than those of 75 and 80 wt%. Thus, it was concluded that 75 and 80 wt% powder loading were inadequate for fabricating photosensitive paste.

Effect of the Type of Monomer. In order to examine the photolithographic properties according to the type of monomer, three Ag pastes were fabricated using three monomers shown in Table II, the test patterns were made with three pastes, and then the fine-line resolutions were analyzed. Ag powder loading was fixed to 70 wt%, KB-2 was used as a

basic binder polymer, binder polymer to monomer ratio was 4:1, and the amount of photoinitiator was 30 wt% of monomer. Test patterns were exposed to UV of 1500 mJ/cm^2 , developed during the time of TTC, and then dried in a convection oven at 80°C .

Figure 9 shows the difference of fine-line resolution after development according to the types of monomers. $20 \mu\text{m}$ patterns were damaged in case of using M300, but M310 showed a well-developed fine-lines. Opposed to M300, the development of $20 \mu\text{m}$ patterns was not completed in the case of M340. This was due to the degree of polymerization of M340. As M340 has 4-functional groups, stronger and


Figure 8. Result of shrinkage matching test with LTCC according to silver content.

Figure 9. Comparison of the development properties as to three monomers : (a) $20\sim 40 \mu\text{m}$ line / space pattern and (b) magnified $20 \mu\text{m}$ line / space pattern.

broader cross-linked polymer chain was formed in the exposed area so that it inhibited the development of fine-line patterns. If longer developing time is applied, it is expected that M340 will also enable 20 μm fine-lines to be formed.

As each monomer has different degrees of polymerization, it is not adequate that the fine-line formation of three pastes is compared and concluded at one exposing dose condition. Therefore, the fine-line formation characteristics according to the exposing dose was investigated, where the exposing dose was changed from 300 to 1,500 mJ/cm^2 with 300 mJ/cm^2 step. The qualitative description of the test results according to monomer and exposing dose is shown in Table III.

When the exposing dose was 300 mJ/cm^2 , all of the patterns were damaged by the developing solution because of insufficient polymerization reaction in the exposed area. Some of the 20 μm line patterns were also washed off the green sheet surface in 600 mJ/cm^2 . Optimum, well-developed fine-lines were obtained from M310 at the exposing dose more than 900 mJ/cm^2 . In case of M340 at 1,500 mJ/cm^2 , the patterns were over-exposed so that the development of fine-line patterns was not completed in the given developing time as described above.

Effect of the Amount of Photoinitiator. A photoinitiator is an important additive of the photosensitive paste in that it forms free radical when exposed to UV and initiates the

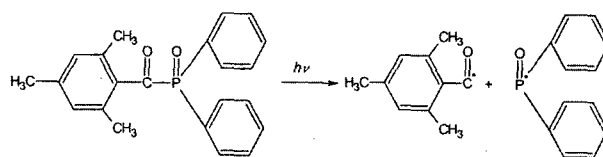


Figure 10. Structure and radical formation of TPO.

polymerization reaction of monomer. Therefore, the control of the amount of photoinitiator in paste is critical. TPO (2, 4,6-trimethylbenzoyl-diphenyl-phosphine oxide) was used in this research because it was known to be one of the acryl phosphine-oxide-type initiators that had excellent absorbing ability around 365 nm UV. Figure 10 shows the structure and radical formation reaction of TPO.²⁰

In order to investigate the photolithographic properties of fine-lines according to the change of TPO amount, five kinds of Ag paste and their test patterns were fabricated. The TPO amount in each paste was 10, 20, 30, 40, and 50 wt% of the monomer amount.

Figure 11 shows the wedge-shape pattern around 25 μm of each test pattern formed on green sheet after development. In the composition of 10 wt% TPO, fine-line was not developed sufficiently because of the insufficient polymerization reaction. In case of 20 wt% TPO, fine-line pattern

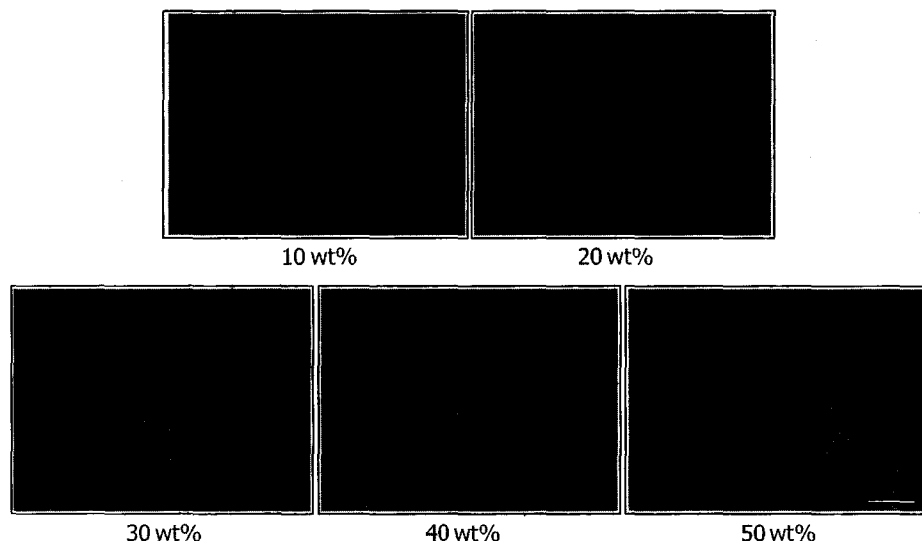


Figure 11. Change of the developed wedge patterns around 25 μm according to the amount of TPO.

Table III. Qualitative Description of the Developed Results According to Exposing Dose

Monomer	Exposure (mJ/cm^2)						Remarks
		300	600	900	1200	1500	
M300		×	△	△	○	○	×
M310		×	△	○	○	○	△
M340		×	△	○	○	△	○

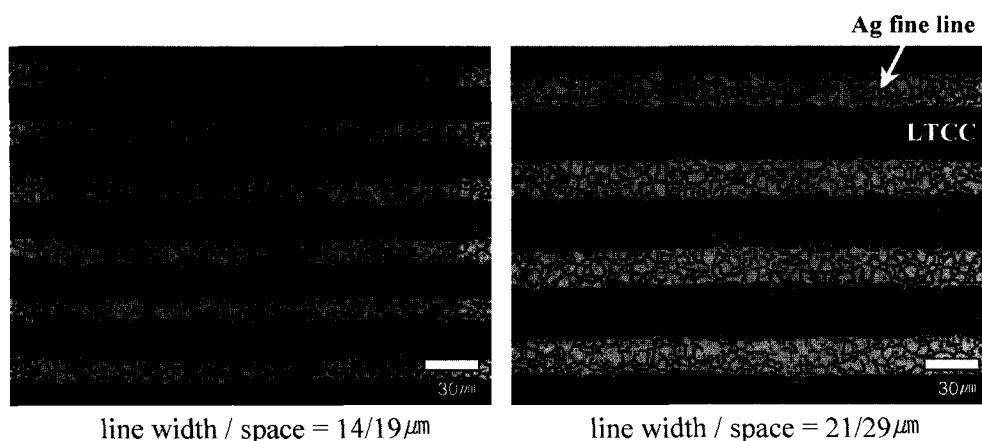


Figure 12. Photographs of thick-film fine line on LTCC after cofiring.

was formed up to $25\ \mu\text{m}$ resolution, but the lines under $25\ \mu\text{m}$ were detached from green sheet surface. Ag paste with 30 wt% TPO showed good resolution below $25\ \mu\text{m}$ line width. With increased TPO amount than 30 wt% of monomer weight, no distinguishable increase in resolution was detected as the amount of monomer consumed in the polymerization reaction was fixed. As the residual photoinitiator not participating in the polymerization reaction has the possibility to degrade the properties of the dried paste layer, 30 wt% of monomer was concluded to be the optimum amount of TPO.

Figure 12 shows the optical photographs of the cofired fine-line patterns of finally selected Ag paste composition; KB-2 was used as acrylic binder polymer, M310 as monomer, Ag loading was 70 wt%, the ratio of polymer to monomer 4:1, and TPO amount 30 wt% of monomer. Fine-lines corresponding to 20 and $30\ \mu\text{m}$ patterns on glass mask were observed using a Nikon microscope, MM-40. Obtained line width after cofiring was measured to be 14 and $21\ \mu\text{m}$, which cannot be fabricated via general screen printing process. Therefore, the result of this experiment sufficiently proved the excellence of thick-film photolithography in obtaining fine lines.

Conclusions

In this research, the development of low-temperature cofireable photosensitive silver paste for fabricating thick-film fine line using the photolithographic technology was conducted. Effects of several parameters including organic compositions or processing conditions on the photolithographic properties of photosensitive Ag paste were investigated. From the results, the optimum amount and ratio of Ag powder loading, the types of acrylic binder polymer and monomer, the amount of photoinitiator, the exposing dose, etc. were determined and the thick-film fine-lines with width under $20\ \mu\text{m}$ were obtained.

Additional research is necessary regarding several untested parameters such as the shape or size of Ag powder, the viscosity of Ag paste, the thickness of dried paste, and so on. From the continuous future researches about the photosensitive paste, it is expected that new materials and technologies can be provided for the fabrication of the highly miniaturized components or modules for high frequency applications.

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