

Effects of the Binder Polymer and Powder Type on the Resolution and Edge Curl of a Silver Electrode Formed by a Photolithographic Process

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ABSTRACT: Silver (Ag) electrodes with a high resolution and a low edge curl dimension for plasma display panels were successfully fabricated through a photolithographic process using photosensitive Ag pastes with several polymeric binders. The gap and line resolutions of the photosensitive Ag pastes were examined as a function of the molecular weights and acid values of the acrylic binders with carboxylic acid groups. The effect on the formation of edge curls was also investigated with dry- and wet-processed Ag powders. Ag electrode patterns with a line resolution of 20 μm , a gap reso-

lution of 40 μm , and an edge curl dimension of 0.8 μm could be achieved with the developing process in 34.5 s (break point \times 1.5) when the photosensitive Ag paste was prepared with the polymeric binder with a molecular weight of 23,320 g/mol and an acid value of 94.98 mg of KOH/g of polymeric binder and with dry-processed Ag powder. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2248–2255, 2009

Key words: lithography; photopolymerization; photoresists; radiation

INTRODUCTION

Conductive patterns formed by the printing process have been widely used in electronic devices such as radio frequency identifiers, solar cells, batteries, sensors, printed circuit board components, and displays.^{1–4} This is due to the merits of printing technology, including lower investment for production equipment, applicability to larger areas, and easier thickness control of the conductive pattern. In these days, various printing technologies such as nanoimprinting, ink-jet printing, gravure printing, photolithographic printing, and offset printing have been studied for application to the fabrication of display panels and other electronic devices.^{5–8} For example, screen printing for barrier ribs in a plasma display panel (PDP) has been replaced with the photolithographic method, and the use of ink-jet printing as a substitute for the photolithographic method

is being examined to fabricate color filters for liquid-crystal displays (LCDs).^{9,10}

PDPs and LCDs are currently competing to lead the market in the production of large-screen televisions greater than 40 in. PDP manufacturers are trying to develop higher resolution and larger screen panels to increase their market share.¹¹ To realize large, high-resolution PDPs, it is necessary to use adequate printing techniques to form some patterns on the front and/or rear panels. As the size of PDPs increases over 60 in., silver (Ag) electrodes with a high resolution and no edge curls are required. Currently, two methods, screen printing and photolithography, are being used to form Ag electrodes with a thickness of 5–10 μm .^{12,13} Screen printing, in which the electrode paste is coated to a surface through a fine-mesh screen with a squeegee, is a stencil printing method. Despite having a couple of advantages such as lower material costs and a simpler process, this technology is considered to be unsuitable for high-resolution patterns because of various controllability issues, such as the printing speed, pressure, material viscosity, and angle of the squeegee, and traces of screen mesh due to the mesh count and material. On the other hand, the photolithographic process,

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comprising coating of the photosensitive Ag paste, drying, ultraviolet (UV) radiation, and developing to produce electrode patterns, is usually used by PDP makers because it is more favorable for high resolution and the production of large panels. However, it is difficult to form electrode patterns under a 50- μm pattern width by the photolithographic method for two reasons: (1) the undercut by overdevelopment in the lower edge part of the electrode pattern can bring about decreasing adhesion strength to the sustain electrode, and (2) edge curl, which occurs in the upper edge part after firing, can cause an electronic breakdown of the localized electric current and also produce bubbles during the formation of the dielectric layer.

In addition to the formation process, the materials used are also important for producing Ag electrodes with a high resolution. The Ag paste for electrode patterns produced by the photolithographic method consists of a functional phase, vehicle, and additives. The functional phase, containing a metal power (Pt, Pd, Ag, Au, etc.) and glass frit, is the main component of the electrode patterns. The vehicle contains a volatile liquid, which is removed during the drying process, and a nonvolatile polymeric binder, UV-curable monomers, and a photoinitiator, which are burned out during the firing process. Additives are used to control the rheological behavior during the coating process. Ag electrode qualities such as pattern sharpness, undercuts, and edge curls are mainly affected by the composition of the Ag paste, especially the Ag particles and binder polymer.

In this study, several polymeric binders for the Ag paste were synthesized, and the characteristics of pattern formation with the molecular weights and acid values of the binders were examined. The effects of different classes of Ag powders on the formation of edge curl were also investigated.

EXPERIMENTAL

Materials

Ag powder and glass frit as the functional phase were used to prepare the photosensitive Ag paste. Two kinds of Ag powders were used. One was a dry-processed Ag powder (D-Ag), and this meant that the Ag powder was made by a dry process. The other was a wet-processed Ag powder (W-Ag). D-Ag (average particle size; $D_{50} = 1.5 \mu\text{m}$) was donated by Kornatech Co. (Changnyoung, Korea), and W-Ag ($D_{50} = 1.6 \mu\text{m}$) was purchased from Aldrich Co. (St. Louis, MO). Glass frit (PbO–B₂O₃–SiO₂–ZnO system) with a 1.3- μm average particle size and a glass-transition temperature of 439°C was obtained from Phoenix PDE Co. (Gumi, Korea) and used as received.

Chart 1 shows the chemical structures of the polymeric binder, UV-curable monomers, and dispersant used in this study. The polymeric binders [i.e., poly(isobutyl methacrylate-co-methacrylic acid-co-2-hydroxyl ethyl methacrylate)s [poly(iBMA-co-MAA-co-HEMA)s]] were prepared through the copolymerization of comonomers such as isobutyl methacrylate (iBMA), 2-hydroxyl ethyl methacrylate (HEMA), and methacrylic acid (MAA). The comonomers were purified to remove inhibitors and moisture and then distilled *in vacuo* before use. α,α' -Azobisisobutyronitrile (Junsei Co., Kyoto, Japan), used as a free-radical initiator, was reagent-grade and was recrystallized from methanol before use. Methanol (TCI Co., Tokyo, Japan) for the polymerization was distilled *in vacuo*, and mercaptoacetic acid (Aldrich) was used as a chain-transfer agent (CTA) for controlling the molecular weights of the polymeric binders.¹⁴ UV-curable monomers such as pentaerythritol triacrylate (PETA), trimethylol propanetriacrylate (TMPTA), and trimethylolpropane ethoxytriacrylate (TMPEOTA) and a benzophenone derivative (HSP-188), used as a photoinitiator, were obtained from SK-CYTEC Co. (Ulsan, Korea) and used as received. *n*-Octadecyltriethoxy silane (TCI) was used as the dispersant for the photosensitive Ag pastes.

Fabrication of the photosensitive Ag paste and photolithographic process

The preparation of the photosensitive Ag pastes and the photolithographic process were carried out in a clean room to avoid dirt contamination. First, the photosensitive Ag pastes were made by the dispersion of the photosensitive vehicle, which was composed of poly(iBMA-co-MAA-co-HEMA) as the binder (7.6 wt %), methanol as the solvent (14.1 wt %), and UV-curable monomers (7.2 wt %) such as PETA, TMPTA, and TMPEOTA, HSP-188 as the photoinitiator (15 wt % on the basis of the reactive monomers), and *n*-octadecyltriethoxy silane as the additive dispersant (1.1 wt %) into a Ag powder (66.5 wt %)/glass frit (3.5 wt %) mixture with a mechanical stirrer, and this was followed by three-roll milling (model 50, Exakt, Hamburg, Germany) for 2 h. Second, the Ag electrodes were formed by the photolithographic process. The photosensitive Ag paste was coated onto a glass substrate through a screen mesh (Stainless no. 325, Newtech Co., Daejeon, Korea) by a screen printer (Newtech) and dried at 110°C in an IR oven for 15 min. Then, a photomask for measuring the resolution and edge curl was placed on top of the dried Ag paste layer and exposed to UV light of 300 mJ/cm² [light intensity (20 mW/cm²) \times exposure time (15 s)]. After UV exposure, the Ag layer was developed with a 0.3 wt % Na₂CO₃ alkaline aqueous solution at 30°C and at a spray pressure of 1.0 kg/cm² by development

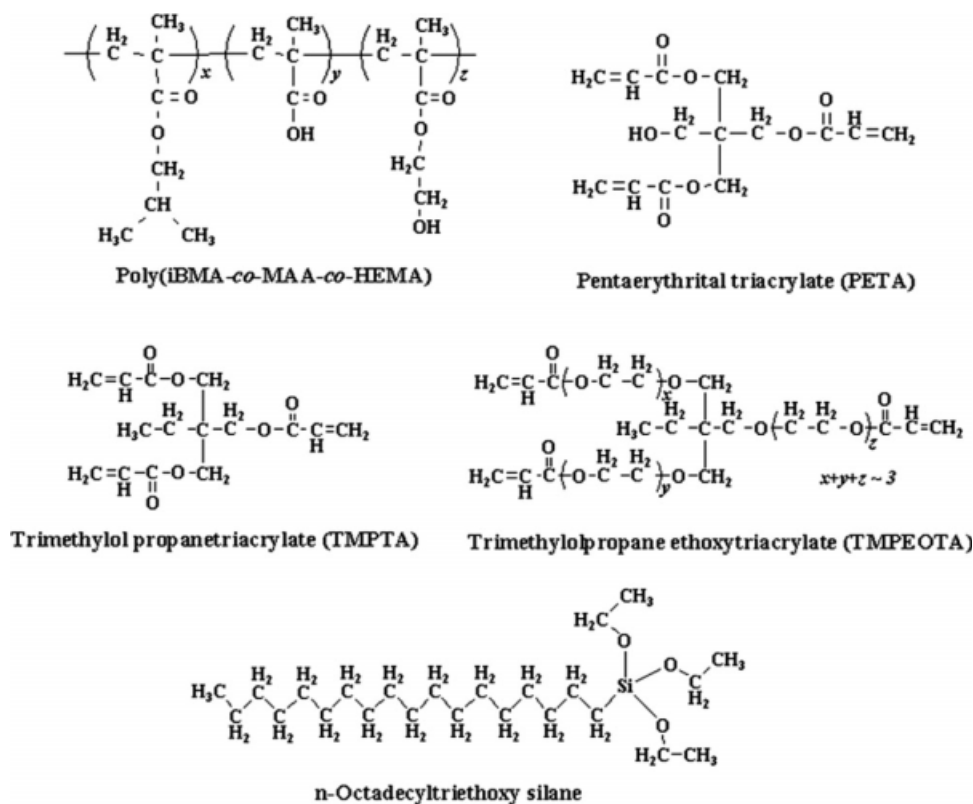


Chart 1 Chemical structures of the polymeric binder, photoreactive monomers, and dispersant.

equipment (YS-Tech, Kumi, Korea) and then dried at 100°C in an oven for 10 min. The development time for the resolution test was fixed as the break point (BP) \times 1.5 s, and the development time for the edge-curl test was changed from BP \times 1.5 to BP \times 4.0 s; BP was defined as the time that it took for an electrode pattern to be peeled off from the glass substrate. The patterned electrode was fired in an electric furnace at 580°C for 30 min at a heating rate of 0.8°C/min to burn out organic materials completely.

Photomask for measuring the resolution and edge curl

To evaluate the resolution and edge curl, three different photomasks were designed and fabricated by Micro Image Co. (Choengwon, Korea). Photomask I (PM-I), used for the evaluation of the gap resolution, had transparent and repeating lines (or patterns) with a width of 800 μ m, and the distance between adjacent repeating lines (e.g., the opaque part) was varied from 300 to 100 μ m (the decrement per line was 10 μ m) and from 100 to 10 μ m (the decrement per line was 10 μ m). In the case of photomask II (PM-II), which was used for the evaluation of line resolution, the width of the transparent lines was varied from 100 to 5 μ m (the decrement per line was 5 μ m), and the width of the opaque lines was set to be 100 μ m. Photomask III (PM-III), used for the eval-

uation of the edge curl, had transparent and repeating lines with a width of 85 μ m.

Instrument analysis

The molecular weights and molecular weight distributions of the synthesized polymeric binders were measured with a Waters gel permeation chromatograph (Milford, MA) using tetrahydrofuran as the eluent. The acid value of the polymeric binders was measured by titration of the binder solution in a mixed solvent (toluene/ethanol = 1/1 v/v) with a 0.1N KOH solution in the presence of 1.0% phenolphthalein, which was used as an indicator (ASTM D 4662). Resolution images of the electrode pattern were investigated with an optical microscope (STM6, Olympus, Tokyo, Japan). Both images and dimensions of the edge curl were examined with scanning electron microscopy (SEM). Electrode patterns were pretreated with Au deposition to obtain SEM images, and the acceleration voltage of SEM was 15 kV.

RESULTS AND DISCUSSION

Properties of the polymeric binders

The general function of polymeric binders is the formation of optimized patterns in a paste, in which these patterns are formed by the development of

TABLE I
Characteristics of Polymeric Binders Synthesized with Different Feed Ratios of the Monomers

Group		iBMA : HEMA : MAA feed ratio (mol)	Initiator (mol)	CTA (mol)	M_w (g/mol)	Acid value (mg of KOH/g of polymer)
A	EBP-1	1.48 : 0.23 : 0.67	0.3	0.2	17,290	79.08
	EBP-2	1.43 : 0.23 : 0.77	0.3	0.2	16,330	84.52
	EBP-3	1.39 : 0.23 : 0.84	0.3	0.2	14,540	90.49
	EBP-4	1.35 : 0.23 : 0.91	0.3	0.2	13,550	97.68
	EBP-5	1.31 : 0.23 : 0.98	0.3	0.2	12,680	106.55
B	EBP-6	1.48 : 0.23 : 0.67	0.2	0.2	26,830	79.44
	EBP-7	1.43 : 0.23 : 0.77	0.2	0.2	25,100	83.77
	EBP-8	1.39 : 0.23 : 0.84	0.2	0.2	24,600	88.98
	EBP-9	1.35 : 0.23 : 0.91	0.2	0.2	23,320	94.98
	EBP-10	1.31 : 0.23 : 0.98	0.2	0.2	22,820	104.92

M_w = weight-average molecular weight.

UV-unexposed areas with an alkali solution.¹⁴ Therefore, polymeric binders were prepared to investigate the effects of the molecular weights and acid values on the line resolution. To make polymeric binders with different acid values, the polymerization of the polymeric binders was performed with changes in the feed ratios of the monomers. Moreover, to investigate the effects of the molecular weights, the initiator/CTA feed ratio was changed from 0.3/0.2 (group A) to 0.2/0.2 (group B), and this resulted in polymeric binders of group A (in a molecular weight range of 12,689–17,290 g/mol) and group B (in a molecular weight range of 24,320–26,830 g/mol) with an acid value range of 79.08–106.55 mg of KOH/g of polymeric binder, which depended on the content of MMA, as presented in Table I.

To determine the optimum development time and to investigate the effects of the molecular weights and acid values of the polymeric binders on the formation

of the Ag electrode pattern, photosensitive Ag pastes using synthesized polymers were prepared with the method described in the Experimental section, and then photolithographic processes were conducted. The BPs, depending on the molecular weights and acid values of the polymers, were measured. With increasing acid value, the BPs were decreased from 98 to 8 s for group A and from 130 to 18 s for group B. These results indicated that the solubility of the synthesized polymers in aqueous Na_2CO_3 solutions was increased with increasing acid value (e.g., with increasing content of carboxylic acid in the polymer chain). With a low acid value, the difference in the BPs with the molecular weight was much greater than with a high acid value, and this indicated that the solubility of the polymer with the high acid value was scarcely affected by the molecular weight. Figure 1 presents the effects of the molecular weights and acid values of the polymeric binders on the BP.

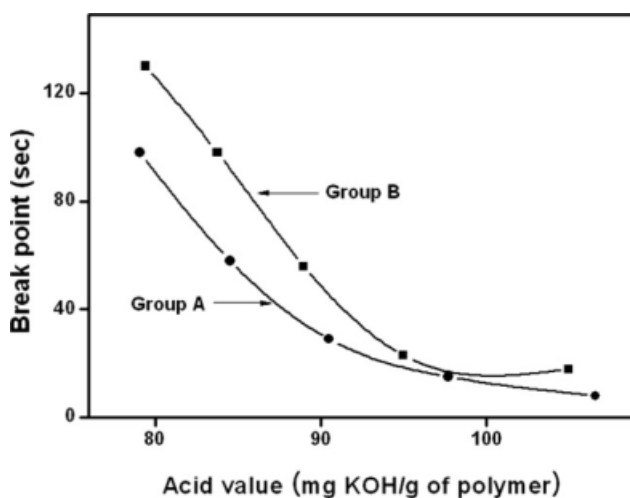


Figure 1 Effect of the molecular weight and acid value of the polymeric binder on the BP.

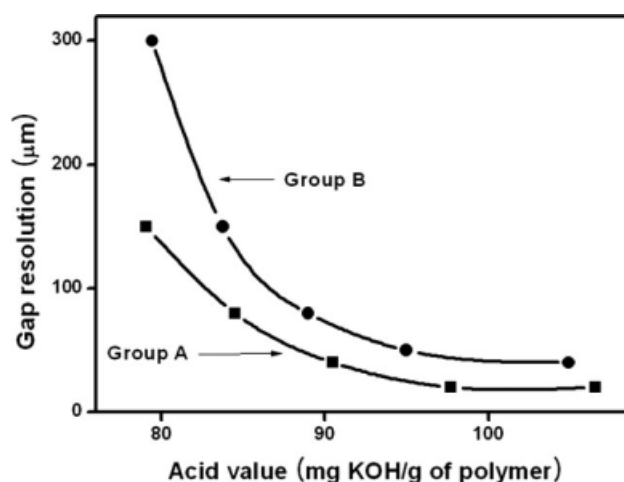


Figure 2 Effect of the molecular weight and acid value of the polymeric binder on the gap resolution.

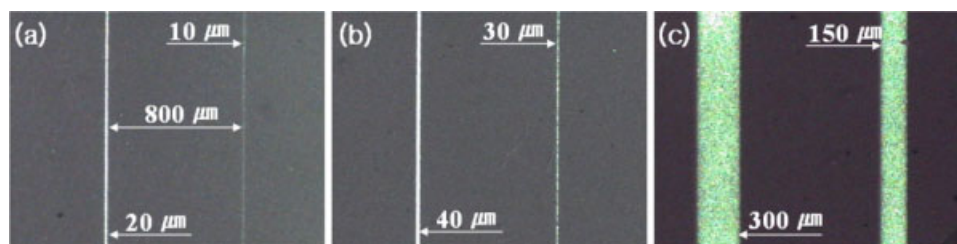


Figure 3 Pattern images of the gap resolution formed with (a) EBP-5, (b) EBP-10, and (c) EBP-1. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Gap resolution with the acid values and molecular weights of the polymeric binders

In the electrode patterns, control of the gap width is necessary to realize high-resolution and large PDPs; *gap* means the space between adjacent repeating lines. The miniaturized gap can contribute to integrating an electric circuit and to preventing an electric short by Ag migration causing a voltage-driving force. The gap width in electrode patterns is usually influenced by the polymeric binder, Ag powder, and photolithographic process conditions. Therefore, the effects of various molecular weights and acid values of the used polymeric binders on the gap resolution were investigated. The photosensitive pastes were prepared with the synthesized polymeric binders, and then the electrodes were formed by the fixed photolithographic process presented in the Experimental section; PM-I as the photomask was used in the UV-exposure process.

Figure 2 presents the results for the effects on the gap resolution (the measured distance between adjacent repeating lines) with the molecular weight and acid value of the binder polymer. The gap resolution was changed from 150 to 20 μm for group A and from 300 to 40 μm for group B. These results mean that the gap resolution is improved with an increas-

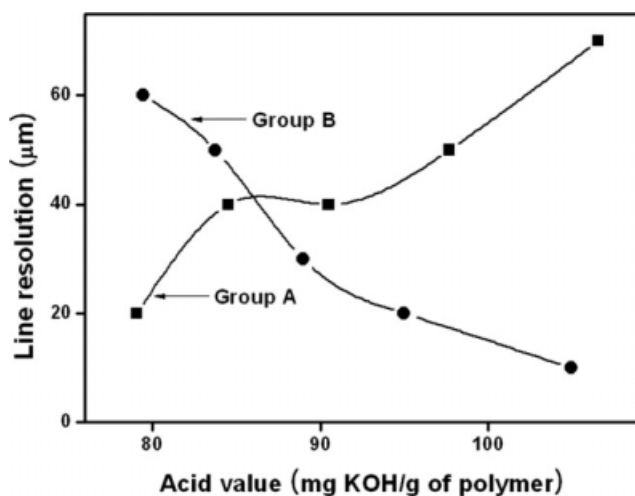


Figure 4 Effect of the molecular weight and acid value of the polymeric binder on the line resolution.

ing acid value because of the solubility of the polymeric binders. Figure 3 presents photographs of gap-resolution patterns with the molecular weight and acid value. When EPB-5 and EPB-10 with high acid values were used, gap-resolution patterns with 20- and 40- μm line spaces were formed, as illustrated in Figure 3(a,b). In the case of EPB-1 with a low acid value, a gap-resolution pattern with 300- and 150- μm line spaces was formed incompletely with some residue, as shown in Figure 3(c). With EPB-6 used as the binder polymer, a gap-resolution pattern with a 300- μm line space was not formed.

Line resolution with the acid value and molecular weight of the polymeric binders

A high resolution means a smaller cell pitch; this makes people appreciate the good image, and the screen image is expressed more delicately. Therefore, miniaturized line width can contribute to integrating an electric circuit and to fabricating a high-resolution PDP. The line width in electrode patterns is usually influenced by the polymeric binder, Ag powder, and photolithographic process conditions. Effects on the line resolution, through the variation of the molecular weights and acid values of the polymeric binders, were investigated with the fixed photolithographic process presented in the Experimental section; PM-II as the photomask was used in the UV-exposure process.

The tendency of the line resolution was different from that of the gap resolution, as illustrated in Figure 4. With increasing acid value, the line resolution of the electrode patterns varied from 60 to 10 μm for group B. In contrast, the line resolution for group A varied from 20 to 70 μm with increasing acid value. Consequently, group B was more advantageous than group A for forming high-resolution electrode patterns. To obtain a high-resolution pattern with a negative-type photoresist, the exposure area should have low solubility, and the nonexposure area should have high solubility. These requirements were well satisfied in group B with a higher molecular weight. In the case of group A with a lower molecular weight, the line resolution deteriorated with

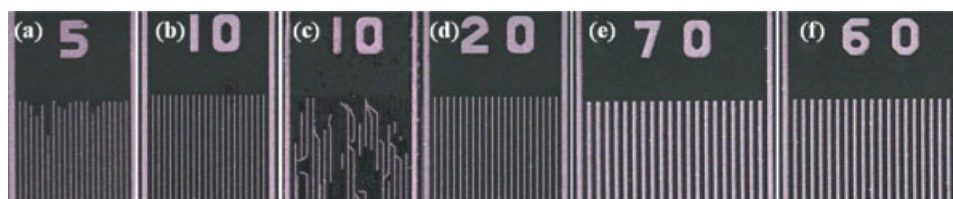


Figure 5 Pattern images of line resolution formed with (a,b) EBP-10, (c,d) EBP-1, (e) EBP-5, and (f) EBP-6. The digits indicate the pattern width of the micrometer unit. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increasing acid value. This seems to have been due to a higher tendency to swell in the UV-exposure area in comparison with group B. Even though polymeric chains are crosslinked in the UV-exposure areas, solvents can swell the crosslinked polymers and then weaken the strength of adhesion to the substrate, and this results in the electrode patterns being peeled off from the substrate. The binder polymers crosslinked from a low molecular weight are more likely to swell. Figure 5 presents the photographs of line-resolution patterns with various molecular weights and acid values. When EPB-10 with a high molecular weight and acid value was used, the electrode pattern with a 5- μm line width was partially peeled off; in contrast, it was excellent at a 10- μm line width, as illustrated in Figure 5(a,b). In the case of EPB-1 with a low molecular weight and acid value, the minimum width without peeling off was 20 μm , as shown in Figure 5(c,d). With EPB-5 and EPB-6 as the binder polymers, the minimum widths without peeling off were 70 and 60 μm , as shown in Figure 5(e,f), respectively.

Changes in the edge curl dimension with the surface morphology of the Ag powder

Spherical Ag powders are usually used to produce the electrode patterns formed by screen printing because the spherical type is superior for moving

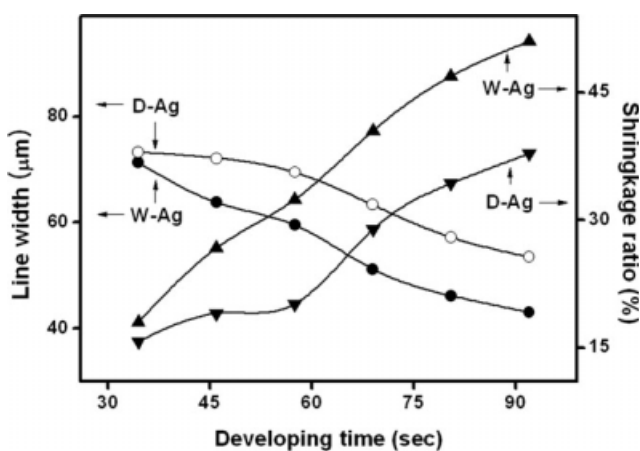


Figure 6 Relations of the line width, shrinkage ratio, and development time with the Ag powder type.

through a screen mesh. In the case of the photolithographic process, the surface roughness of a spherical Ag powder can affect the sharpness and edge curl of the electrode pattern. It is well known that D-Ag has lower surface roughness than W-Ag. With D-Ag and W-Ag, bus electrode patterns were formed to compare the effect of surface roughness on edge curl. Ag pastes were prepared with EBP-9 as the polymeric binder, showing both good line (20 μm) and gap (40 μm) resolution, and then a photolithographic process using PM-III as a photomask was conducted. The development time was varied from 34.5 (BP \times 1.5) to 92.0 s (BP \times 4), and the changes in the line width, shrinkage, and edge curl were monitored before and after the firing process.

The resulting line widths and their shrinkage ratio [100 - (line width after firing/line width before firing) \times 100] with the development times are shown in Figure 6. The line widths before firing were almost constant (ca. 88 μm), regardless of the type (e.g., surface roughness) of Ag powder. After firing, the line widths were reduced from 71.3 to 43.1 μm for W-Ag and from 73.3 to 53.5 μm for D-Ag with increasing development time. The electrode pattern formed with D-Ag showed a broader width than that formed with W-Ag with the same development time, and the change in the shrinkage ratio in D-Ag

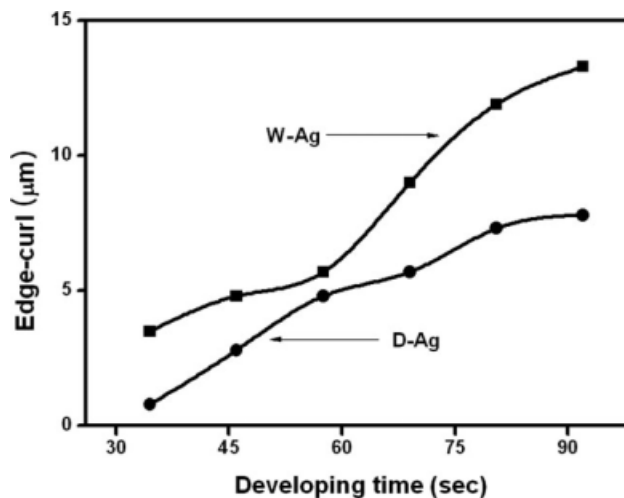


Figure 7 Edge curl dimension with the development time and Ag powder type.

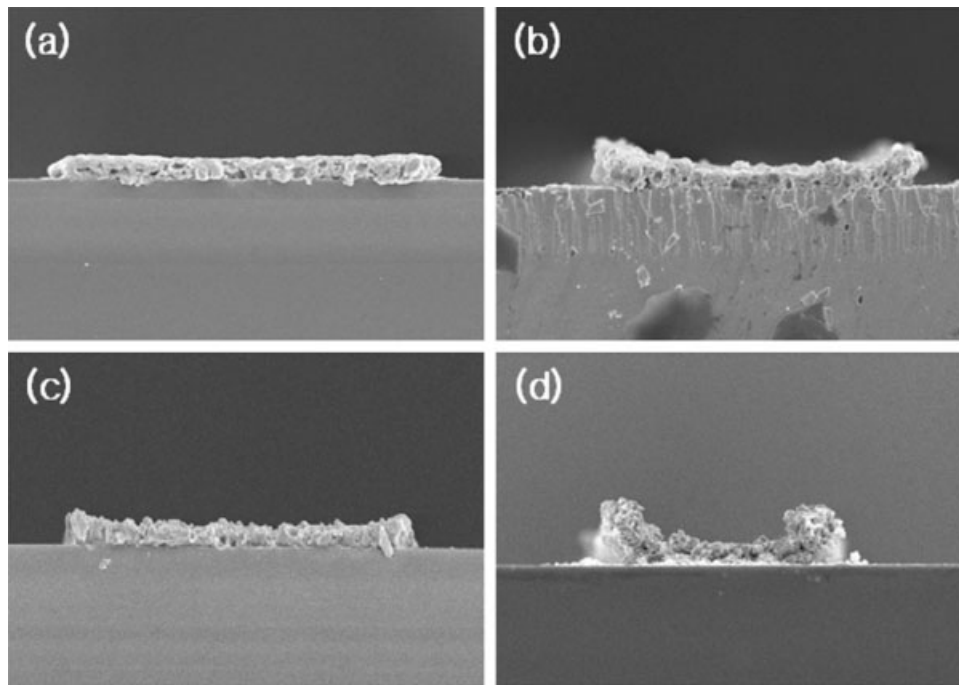


Figure 8 Edge curl images magnified 500,000 times with the Ag powder type and development time: (a) D-Ag and 34.5 s, (b) D-Ag, 92.0 s, (c) W-Ag and 34.5 s, and (d) W-Ag and 92.0 s.

(from 15.7 to 37.8%) was smaller than that in W-Ag (from 18.0 to 51.0%).

As shown in Figure 7, the edge curl dimensions increased from 3.5 to 13.3 μm (W-Ag) and from 0.8 to 7.8 μm (D-Ag) with increasing development time, and the edge curl dimension was defined as follows:

(maximum thickness after firing in the edge part of the electrode pattern) – (average thickness after firing in the middle part of the electrode pattern). Figure 8 illustrates edge curl images with the Ag powder types and development time, indicating that D-Ag was more favorable for reducing the edge curl

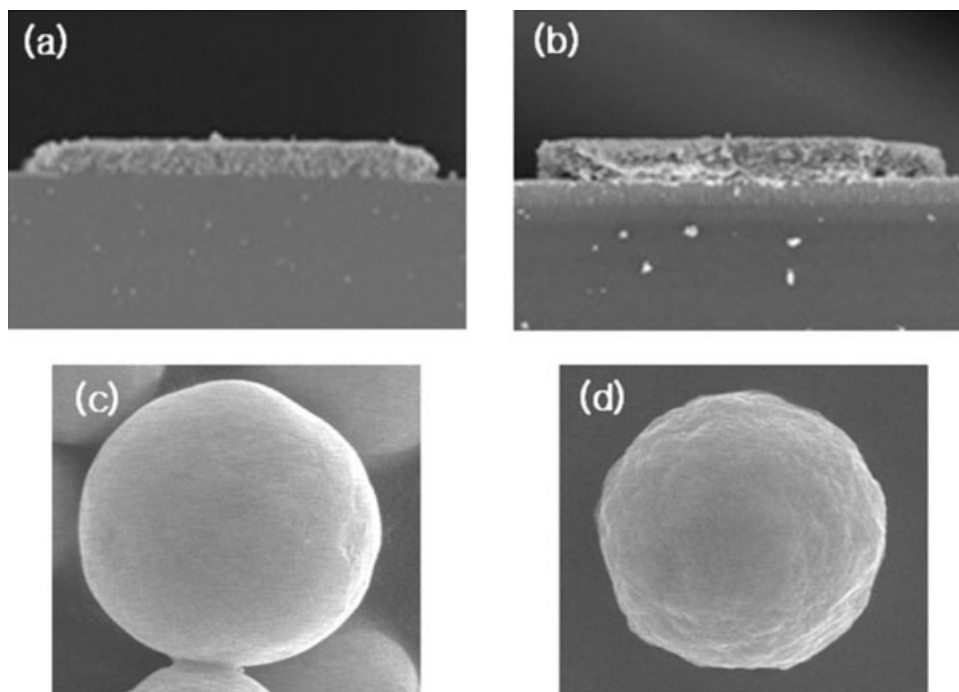


Figure 9 SEM images of the undercut formed with (a) D-Ag and (b) W-Ag and images of the surface roughness of (c) D-Ag and (d) W-Ag. For the undercut images, the development time was 46 s, and all the images were magnified 500,000 times.

dimension. These results, including the low shrinkage ratio and low edge curl dimension in D-Ag, might be due to the absence of air between Ag particles. When W-Ag was used, air could exist on the Ag surface because of the high surface roughness, and this resulted in radical quenching by oxygen during photopolymerization. It can be concluded that a low degree of polymerization or crosslinking can weaken resistance for the developer; as a result, problems such as shrinkage, edge curl, and undercut are generated. This inference is supported by the SEM images of electrode patterns and the surface roughness of Ag particles, as presented in Figure 9.

CONCLUSIONS

Electrode patterns with a high resolution were investigated to realize high-definition PDPs. Photosensitive Ag paste was formulated with several polymeric binders because the line and gap resolutions of electrode patterns of PDPs were affected by the molecular weights and acid values of the acrylic binders with carboxylic acid groups. This study showed that the gap resolution was improved with increasing acid value, regardless of the molecular weights. With increasing acid values, the line resolution was improved with relatively high molecular weights; however, the line resolution deteriorated with relatively low molecular weights because of the relationship between the solubility and adhesion strength. The effect on the formation of edge curl was also investigated with both dry- and wet-processed Ag powders. As a result, when the photosensitive Ag pastes were prepared with the polymeric

binder (EPB-9) with a molecular weight of 23,320 g/mol and an acid value of 94.98 mg of KOH/g of polymeric binder and with D-Ag, a line resolution of 20 μm , a gap resolution of 40 μm , and an edge curl dimension of 0.8 μm could be achieved under the developing conditions in $\text{BP} \times 1.5$. These results can be expected to be used not only for electrode patterns in high-resolution PDPs but also in other electronic components.

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