

# Photosensitive Barrier Rib Paste for Plasma Display Panel and Photolithographic Process

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**ABSTRACT:** Barrier ribs in color plasma display panels (PDPs) function to maintain the discharge space between two glass plates as well as to prevent optical crosstalk. Patterning of barrier ribs is one of the unique processes for making PDPs. In this work, photosensitive barrier rib pastes were prepared by incorporating binder polymer, solvent, functional monomers, photoinitiator, and barrier rib powder. Studies of the function of the materials for the barrier rib paste were undertaken. After optimization of the paste formulation and photolithographic process, the barrier rib could be obtained with good resolution up to 110–120  $\mu\text{m}$  height and 80–90  $\mu\text{m}$  width. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2092–2099, 2002

**Key words:** lithography; photopolymerization; rheology

## INTRODUCTION

Plasma display panel (PDP) is considered to be the most promising option for a large size (> 40 in.), flat panel display. PDP is based on the photoluminescence phenomena occurring on the red, green, and blue phosphor layers due to vacuum ultraviolet (UV) light (mainly 147 nm) generated by the penning gas mixture in the surface-discharged plasma cell.<sup>1–3</sup> A schematic diagram of the alternating current (AC) type color PDP is shown in Figure 1.

Barrier ribs in the color PDP are indispensable to maintain the discharge space between two glass faceplates as well as to prevent optical crosstalk in adjacent cells.<sup>4</sup> These ribs are endowed with the function of retaining uniform discharge spaces, because of their own height, width, and pattern gap, and enhancing the mechanical strength of the whole panel.<sup>5–7</sup> It is necessary to

form barrier ribs that have a large aspect ratio and sufficient strength to provide the performance necessary for the proper functioning of PDP.

The formation of barrier ribs is one of the unique processes for making PDP and has a large effect on the performance. The barrier ribs currently employed are typically 110–120  $\mu\text{m}$  in height, with upper and lower widths of 50 and 80  $\mu\text{m}$ , respectively, and a pitch of 300  $\mu\text{m}$ . Various means to form barrier ribs in the PDP, such as screen printing and sandblasting, are known. However, screen printing has the disadvantage of poor workability and application to large size PDP. Thus, the feasibility of a photolithographic process has been under study recently. In this process, photosensitive barrier rib paste is coated on the rear glass panel of PDP and dried. After UV exposure through photomask and development, the barrier rib pattern is obtained. Then, the panel is subjected to firing up to 550 °C to burn out all organic and polymer materials that took part in the formation of barrier ribs on the PDP.

In this work, photosensitive barrier rib paste was prepared by incorporating binder polymer,

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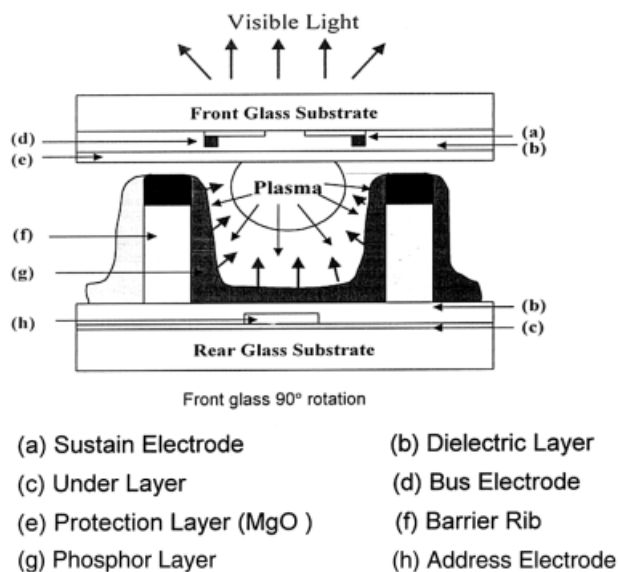


Figure 1 Structure of AC-PDP.

solvent, functional monomers, photoinitiator, and barrier rib powder. The effect of component and concentration of photosensitive barrier rib paste was examined for the optimization of the paste formulation and photolithographic process.

EXPERIMENTAL

Materials

Pentaerythritol triacrylate (PETA) and other UV oligomers, such as trimethylolpropane triacrylate (TMPTA), tripropylene glycol diacrylate (TPGDA), and bisphenol A epoxy diacrylate (EB 600), were obtained from SK-ucb Company and used as received. Butyl carbitol (BC) as solvent, methyl methacrylate (MMA), and methacrylic acid (MAA) were purchased from Aldrich Chemical Company and used without further purification. Tetrahydrofuran (THF) was used after distillation with calcium hydride. 2,2'-Azobisisobutyronitrile (AIBN) initiator from Wako Chemical was purified by recrystallization from methanol. A mixture photoinitiator (HSP 188) was obtained from SK-ucb Company and used as received. Barrier rib powder used in the paste has an approximate composition of PbO 60.0 wt %, SiO<sub>2</sub> 10.7 wt %, Al<sub>2</sub>O<sub>3</sub> 29.0 wt %, and trace (0.3 wt %) amounts of ZrO<sub>2</sub>.

Synthesis of Binder Polymer

MMA monomer was copolymerized with MAA by free radical polymerization at various feed ratios.

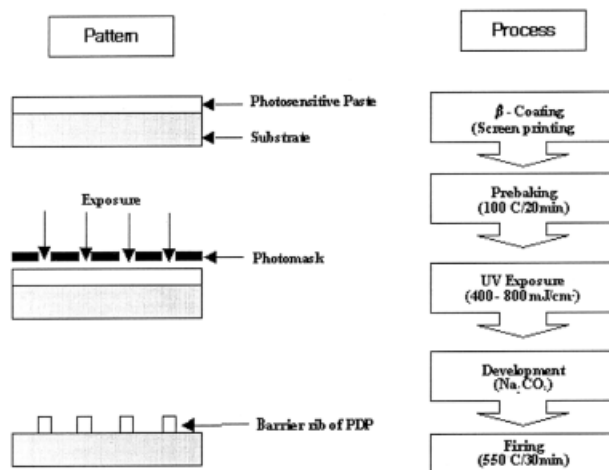


Figure 2 Formation of PDP barrier ribs by a photolithographic process.

Polymerization was conducted at 15 wt % monomers in THF solvent with AIBN as initiator. The reaction mixture was purged thoroughly with nitrogen gas and then stirred for 24 h at 60 °C. The copolymers were recovered by precipitating in hexane, washed, and dried under vacuum overnight before analysis for copolymer composition.

Photosensitive Barrier Rib Paste Formulation and Photolithographic Process

Photosensitive barrier rib paste was made by dispersing barrier rib powder containing glass frit and aluminum oxide into liquid vehicle composed of poly(MMA-co-MAA) binder polymer, BC sol-

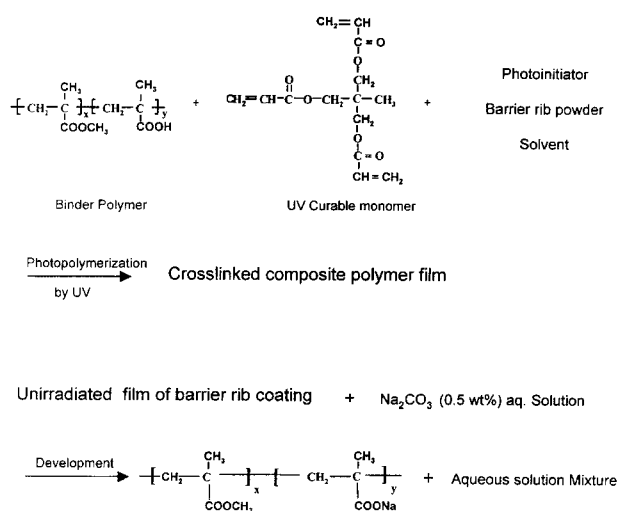


Figure 3 Photopolymerization and developing mechanisms of barrier rib paste.

**Table I Synthesis and Characterization of Poly(MMA-co-MAA) Binder Polymer**

Sample No.	Feed Ratio	Copolymer	Molecular Weight		Yield (%)
	MMA : MAA	MMA : MAA	$M_w$	PDI	
GK-1	90 : 10	84.3 : 15.7	21,400	1.98	90.5
GK-2	80 : 20	78.2 : 21.8	10,900	2.01	92.0
GK-3	80 : 20	75.1 : 24.9	20,000	2.50	91.5
GK-4	80 : 20	76.0 : 24.0	51,100	2.08	93.0
GK-5	80 : 20	74.9 : 25.1	190,000	2.98	92.5
GK-6	50 : 50	53.2 : 46.8	20,500	2.45	92.5
GK-7	30 : 70	19.3 : 70.7	19,900	2.01	93.0

vent, UV crosslinkable monomers, and HSP-188 photoinitiator using a three-roll mill. A laboratory size, three-roll mill (Exakt 50, Germany) was used for the homogeneous mixing of paste component. The viscosity of barrier rib paste was measured with Brookfield viscometer and adjusted to 20,000–29,000 cps range by adding BC solvent.

The formation of barrier rib by photolithographic process using photosensitive barrier rib paste is shown in Figure 2. This process was carried out in a clean room to avoid dirt contamination. The barrier rib paste was coated on the glass substrate with a handy coater with 200–400- $\mu\text{m}$  gap. The thickness of dried barrier rib coating was varied in the range 100–170  $\mu\text{m}$ . The dried barrier rib was exposed to UV light (400–800  $\text{mJ}/\text{cm}^2$ ) through a photomask.<sup>8,9</sup> The optimum exposure time was determined from a series of experiments to yield correct shape and size of barrier rib after development and drying. The UV-exposed barrier rib panel was developed with 0.5 wt % sodium carbonate aqueous solution. The

developing solution was sprayed at  $\sim 20$  psi pressure. The developed barrier rib panel was dried at 100 °C for 20 min. The patterned barrier rib was fired in electric furnace at 550 °C for 30 min to burn out organic materials completely.<sup>10–12</sup>

#### Analysis and Measurements

The nuclear magnetic resonance (NMR) spectra of poly(MMA-co-MAA) samples were recorded on a Bruker 300 MHz  $^1\text{H}$  NMR spectrometer. The molecular weights of binder polymers were obtained by Waters gel permeation chromatograph (GPC) using THF as eluent. Microstructure and barrier rib pattern were examined by scanning electron microscopy (SEM). Barrier rib pattern was pre-treated with Au deposition, and acceleration voltage was 15 kV.

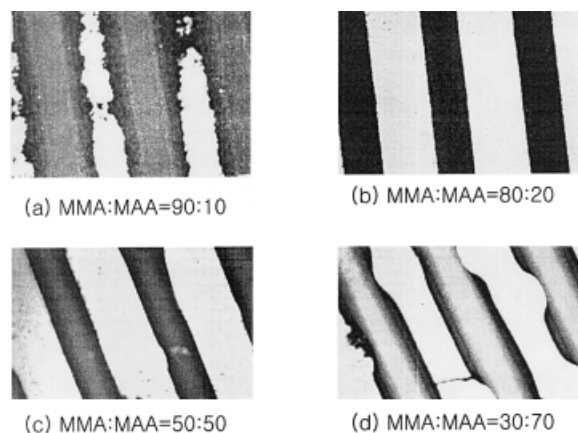
## RESULTS AND DISCUSSION

Barrier ribs in the color PDP are indispensable to maintain plasma discharge spaces between two

**Table II Effect of Binder Polymer on the Photolithographic Patterning of Barrier Ribs**

Device No.	Binder Polymer		Paste Formulation (g)		
	Composition MMA : MAA (mol %)	$M_w$ g/mol (GPC)	Vehicle <sup>a</sup>	Barrier Rib Powder	Barrier Rib Pattern
AD-1	90:10	21,400	4.3	6.5	×
AD-2	80:20	20,000	4.3	6.5	○
AD-3	50:50	20,500	4.3	6.5	×
AD-4	30:70	19,900	4.3	6.5	△
AD-5	80:20	10,900	4.3	6.5	×
AD-6	80:20	51,100	4.3	6.5	△
AD-7	80:20	190,000	4.3	6.5	×

<sup>a</sup> Vehicle consists of binder polymer, solvent, UV monomers, and photoinitiator.



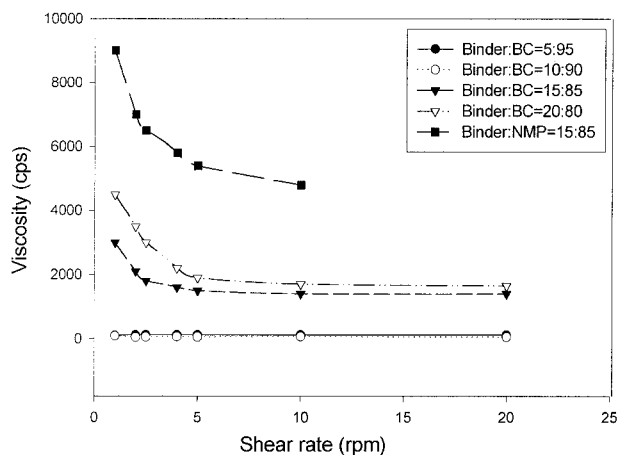
**Figure 4** Photographs of barrier rib fabricated with different composition of binder polymer poly(MMA-co-MAA)s.

glass plates. The barrier ribs with a typical structure of 110–120  $\mu\text{m}$  height, 50–80  $\mu\text{m}$  width, and 300  $\mu\text{m}$  pitch need to be patterned uniformly on the bottom glass plate of PDP in size up to 60 in. diagonally.

The formation of barrier ribs by the photolithographic process is shown in Figure 2. Photosensitive barrier rib paste is coated usually by screen printing on the rear glass panel of PDP and dried in a infrared (IR) chamber. Then the panel is exposed to UV light through patterned mask, and the unexposed areas are developed with aqueous alkaline solution. Various components of barrier rib paste have significant effects on the photolithographic patterning of barrier ribs.

#### Binder Polymer and Solvent for Photosensitive Barrier Rib Paste

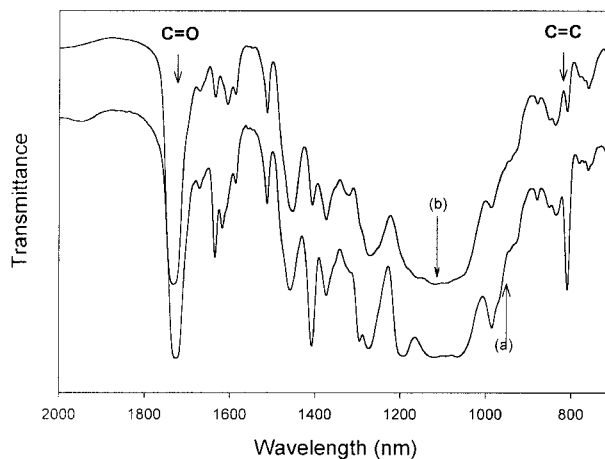
The main components of barrier rib paste include binder polymer, solvent, functional monomers, photoinitiator, and barrier rib powder. The photopolymerization and developing mechanisms of barrier rib paste are shown in Figure 3. The binder polymer itself is not photosensitive. The multifunctional monomers dispersed in the paste are converted to a three-dimensionally cross-linked composite polymer by the action of photoinitiator. In the unexposed area, however, the acidic binder polymer is converted to a carboxylated form, and the whole mixture of barrier rib, including unreacted monomers and UV oligomers, is washed away when developed with the aqueous alkaline solution.



**Figure 5** Effect of solvent and concentration of binder polymer on the rheological property.

The main function of binder polymer is to bind the inorganic barrier rib powders, but it also has effects on the rheology of the barrier rib paste during screen printing and in the development step. The molecular weights, yield, and composition of binder polymers, poly(MMA-co-MAA)s, synthesized are shown in Table I. The binder polymers with weight average molecular weight ( $M_w$ ) of 10,000 to 190,000g/mol and polydispersity indices of 1.98 to 2.98 were obtained when the MMA:MAA copolymer composition was varied from 90:10 to 30:70 mol %. The copolymer compositions determined by  $^1\text{H}$  NMR were close to those of monomer feed ratios.

To select the proper binder polymer, photosensitive barrier rib pastes were made using the typ-



**Figure 6** FT-IR spectra of films obtained from photosensitive vehicles (a) after UV irradiation (400  $\text{mJ}/\text{cm}^2$ ) and (b) before irradiation.

**Table III** Photosensitivity of Vehicle Formulation by FT-IR Analysis

Sample No.	Binder		Monomer/Weight (g)	Oligomer/Weight (g)	Photoinitiator (HSP-188, g)	Residual C=C (mole)	Conversion <sup>a</sup> (%)
	Polymer (GK-3, g)	Solvent (BC, g)					
PRM-1	1.0	3.0	—	EB 600 10.0	0.3	0.057	38.0
PRM-2	1.0	3.0	TPGDA 2.5	EB 600 7.5	0.3	0.046	44.3
PRM-3	1.0	3.0	PETA 10	—	0.3	0.101	58.8
PRM-4	1.0	3.0	TMPTA 10	—	0.3	0.101	69.1
PRM-5	1.0	3.0	TMPEOTA 10	—	0.3	0.070	81.8

<sup>a</sup> Conversion (%) was determined by FT-IR analysis after UV irradiation (450 mJ/cm<sup>2</sup>).

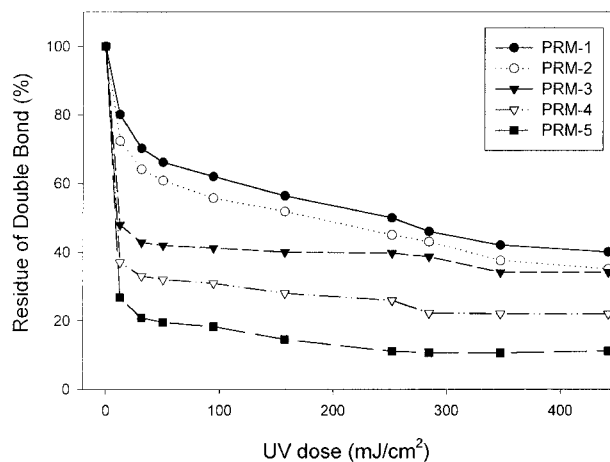
ical formulation (Table IV) discussed later. The effect of  $M_w$  and copolymer composition on the patterning of barrier ribs by photolithographic process is shown in Table II and Figure 4. The copolymer with  $M_w$  of  $\sim 20,000$  g/mol and MAA content of 25 mol % (GK-3) was found to be a useful binder polymer. Copolymers with higher MAA content were developed quickly, and erosion to the exposed area was detected in the barrier rib after development. Formulation of barrier rib paste with binder polymer of  $\sim 25\%$  MAA and  $M_w$  of  $\sim 20,000$  g/mol gave rib pattern with improved sharpness and width uniformity. This result may be due to better dispersion of barrier rib powder in the paste. It is well known that low  $M_w$  copolymers with carboxylate functional group act as dispersants in a slurry mixture containing inorganic particles.<sup>13</sup>

Next we examined the binder polymer/solvent combination. In Figure 5 are shown the viscosity versus shear rate curves of the binder polymer (GK-3)/solvent system. The binder polymer has an effect on the rheological property of barrier rib paste in the screen printing process. Binder polymer (GK-3) in BC at  $\sim 15$  wt % was found to give optimum rheological property. Solvents with relatively high boiling points are preferred in the pastes for PDP to minimize evaporation during printing work, otherwise the rheological property of paste will be changed. *N*-Methyl pyrrolidinone (NMP) gave too high viscosity with the binder polymers at  $\sim 15$  wt % concentration.

#### Photosensitivity of UV-Curable Monomer/Oligomer System

The fine patterning of barrier rib is dependent on many parameters involved in both the formulation of photosensitive barrier rib paste and photolithographic process. One of the important fac-

tors controlling the photosensitivity of barrier rib paste is the selection of UV curable monomer/oligomer system. To compare the photosensitivity of UV curable monomer/oligomer system, photosensitive vehicles that do not contain barrier rib powder were prepared and their photosensitivity was evaluated. The photosensitive vehicles were prepared as following. First, GK-3 binder polymer (1.0 g) was dissolved in 3.0 g of BC solvent. To this solution were added a total of 1.0 g of monomer/oligomer mixture and 0.3 g of photoinitiator (HSP-188). This clear solution was coated on the plane glass by a bar type applicator with the gap of 400  $\mu\text{m}$ . The coated glass was dried in the 90 °C oven for 20 min to remove the remaining solvent. The dried film was then irradiated with UV lamp for different time interval. The UV-irradiated sample was subjected to Fourier transform infrared (FT-IR) spectrophotometric analysis to check the residual C=C double bonds according to the following equation:



**Figure 7** Residue of double bond versus UV dose plots of the photosensitive vehicle formulations.



**Table IV Photosensitive Barrier Rib Formulation and Photolithographic Property**

Barrier Rib Paste	Formulation				Barrier Rib Powder (g)	Irradiation Dose and Pattern Shape				
	Binder (g)	BC (g)	TMPEOTA (g)	Photoinitiator (g)		200 mJ/cm <sup>2</sup>	400 mJ/cm <sup>2</sup>	600 mJ/cm <sup>2</sup>	800 mJ/cm <sup>2</sup>	1000 mJ/cm <sup>2</sup>
	RF-1	0.75	4.25	0.5		0.3	8.72	×	×	×
RF-2	0.75	4.25	1.0	0.3	9.47	×	×	×	△	△
RF-3	0.75	4.25	1.5	0.3	10.22	×	×	△	○	○
RF-4	0.75	4.25	2.0	0.3	10.97	×	△	○	○	○
RF-5	0.75g	4.25	3.0	0.3	12.47	×	△	○	○	○

C=C(%)

$$= \frac{\text{Abs(C=C)/Abs(C=O) [after radiation]}}{\text{Abs(C=C)/Abs(C=O) [before radiation]}} \times 100 \quad (1)$$

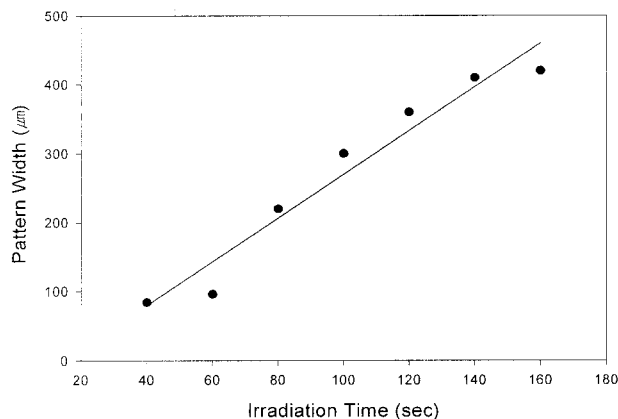
where C=C (%) is the residual double bond, Abs(C=C) is the area of the C=C bond absorption peak (maximum at 821 cm<sup>-1</sup>), and Abs(C=O) is the area of the C=O bond absorption peak (maximum at 1730 cm<sup>-1</sup>).

In Figure 6 are shown the FT-IR spectra of film made from photosensitive vehicles. Spectrum (a) obtained after UV exposure (400 mJ/cm<sup>2</sup>) exhibited a smaller C=C absorption peak at 812 cm<sup>-1</sup> because of the photopolymerization of multifunctional monomer, trimethylolpropane ethoxy triacrylate (TMPEOTA), which was used in the PRM-5 formulation of Table III. Spectrum (b) was obtained from the dry unexposed film utilizing the same formulation. Figure 7 exhibits the plots of the residual C=C double bond (%) versus the dose of UV irradiation (mJ/cm<sup>2</sup>) obtained from the photosensitive vehicle formulations shown in Table III. In Figure 7 the residual C=C double bonds leveled off at a UV dose > 400 mJ/cm<sup>2</sup>, and these values were used as the conversions in Table III. In Table III, EB 600 is a UV oligomer (bisphenol A epoxy diacrylate) of difunctionality. TPGDA, PETA, and TMPTA represent tripropylene glycol diacrylate ( $f = 2$ ), pentaerythritol triacrylate ( $f = 3$ ), and trimethylolpropane triacrylate, respectively. When relatively high  $M_w$ , difunctional EB 600 was used alone, it gave low conversion because of the reduced C=C double bond concentration in the photosensitive vehicle (PRM-1). When a difunctional monomer (TPGDA) was added in the formulation (PRM-2), the con-

version was increased because of the net increase of C=C bond concentration and improved mobility of the formulation.. The trifunctional monomers exhibited even higher conversions. Of the photosensitive vehicles tested, the one with TMPEOTA as UV crosslinkable monomer (PRM-5) gave the highest conversion. This result may be due to the improved compatibility of TMPEOTA with the binder polymer and flexibility of the composite paste film after drying.

### Paste Formulation and Photolithographic Process

As the major components of the barrier rib paste were selected, photosensitive vehicles were mixed with the barrier rib powder, and the photolithographic properties were examined. Photolithographic process consists of screen printing of paste, drying, UV exposure, development, and firing of barrier ribs. Of these processes, UV expo-


**Figure 8** Effect of exposure time on pattern width.

**Table V** Effect of Developer on the Patterning of Barrier Ribs<sup>a</sup>

Solvent	Developing Speed	Sharpness of Barrier Rib	Adhesion to Glass Substrate
KOH	○	△	△
Na <sub>2</sub> CO <sub>3</sub>	○	○	○
NaOH	○	△	△

<sup>a</sup> (○) good; (△) moderate.

sure and development are two important steps for the fine uniform pattern of barrier ribs.

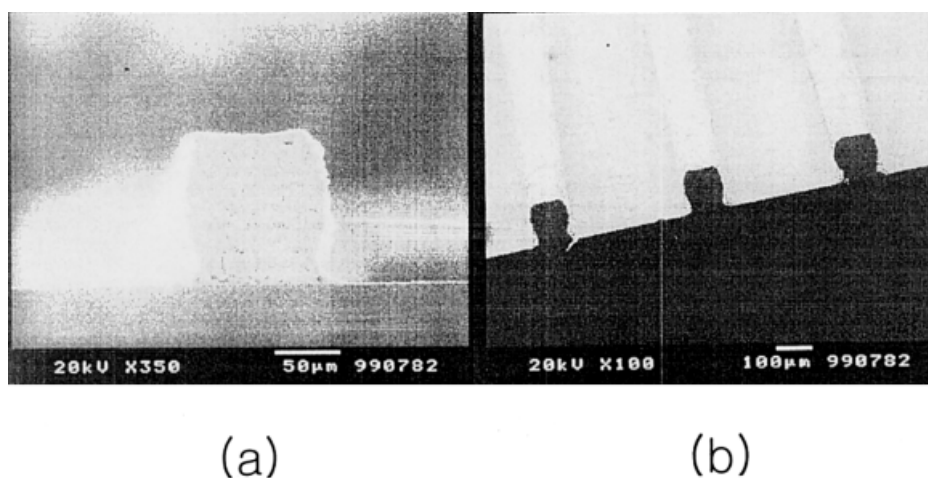
The relationship between the UV dose and patterning quality of barrier ribs obtained with various photosensitive barrier rib pastes is shown in Table IV. Here, the amount of barrier rib powder was kept constant at 60 wt % in the paste and the amount of multifunctional monomer and UV dose were varied. When the amount of multifunctional monomer was insufficient, the barrier ribs were all washed away regardless of the UV dose. When the amount of monomer was above a certain level, even a low dose of UV irradiation could pattern the barrier ribs. However, too much monomer is detrimental because the trace of residual organic materials in the barrier ribs after firing may cause out-gassing problems during the long-term operation of PDP. Thus, the optimum amount of TMPEOTA monomer in the paste formulation was determined to be ~2.0 g, as in the RF-4 formulation. Exposure time is also important. The increase of barrier rib width with the UV exposure time utilizing the RF-4 formulations shown in Figure 8. The barrier rib pattern in Figure

8 was obtained with a mask of 80 μm width, utilizing a 10 mW/cm<sup>2</sup> power UV lamp. Optimum exposure time was ~60 s in this case. The slope of the plot in Figure 8 (80 μm/s) indicated a rather photosensitive paste for the photolithographic operation. This photosensitivity could be further adjusted with the amount of photoinitiator.

Photosensitive barrier rib pastes need to be designed for development with dilute aqueous alkaline solution and spray equipment like in the semiconductor industry to minimize the environmental contamination. As for the formulation of photosensitive barrier rib paste, the binder polymer has a major effect on the uniformity and morphology of barrier ribs in the development step. As discussed earlier, binder polymer with  $M_w = 20,000$  g/mol and MAA content of 25 mol % gave optimum dissolving property in the development step. The selection of aqueous base in the development utilizing paste formulation RF-4 is summarized in Table V. The developer employing Na<sub>2</sub>CO<sub>3</sub> (0.5 wt % aqueous solution) resulted in better adhesion of the barrier ribs than the strong bases such as KOH and NaOH. The SEM images of barrier ribs obtained with the optimized paste formulation and photolithographic processes are shown in Figure 9. A barrier rib pattern with 110–120-μm height, 80–90-μm width, and 300-μm pitch could be obtained.

## CONCLUSIONS

The components needed for the photolithographic patterning of barrier ribs include binder polymer, solvent, UV-curable monomers, photoinitiator,



**Figure 9** SEM photographs of barrier ribs: (a) cross section; (b) top view.

and barrier rib powder. Binder polymer had effects on the rheology of paste in the screen printing and also on the development step. Poly(MMA-co-MAA), with  $M_w$  of 20,000 g/mol and MAA content of 25 mol %, gave good dispersion of paste and development property. The FT-IR analysis of film from photosensitive vehicles was useful for the selection of UV-curable monomers. TMP-EOTA gave good patterning of barrier ribs because of its contribution to the improved compatibility and flexibility in the paste composite film. In the photolithographic process, UV exposure and development were two important parameters for the fine uniform pattern of barrier ribs. Weak developer, employing 0.5 wt %  $\text{Na}_2\text{CO}_3$  aqueous solution, resulted in better adhesion of barrier ribs than strong bases such as KOH and NaOH.

## REFERENCES

1. Jackson, R.N.; Johnson, K.E. *Advances in Electronics and Electron Physics*; Academic: New York, 1974.
2. Park, L. S.; Jeong, S. W.; Oh, H. S.; Kim, S. H.; Song, S. M. *J Korea Ind Eng Chem* 1999, 10, 1114.
3. Mizutani, K.; Kanda, S.; Sone, T. *IDW '96*, 263, 1996.
4. Nguyen, N. T.; Igarashi, K.; Kageyama, H.; Miko-shiba, S. *SID'94*, 319, 1996.
5. Andrzejewska, E.; Andrzejewski, M. *J Polym Sci, Part A: Polym Chem* 1998, 36, 655.
6. Decker, C.; Moussa, K. *Macromol Chem, Rapid Commun* 1990, 11, 159.
7. Lay, F. M.; Chu, C.K. *J Appl Phys* 1973, 44, 4008.
8. Decker, C.; Moussa, K. *Macromol Chem, Rapid Commun* 1991, 12, 507.
9. *Encyclopedia of Polymer Science and Engineering*, 2<sup>nd</sup>. Ed.; Wiley Interscience: New York, 1985; vol. 3, p. 226.
10. Choi, J. H.; Drozdyk, L.P.; Tsuchiya, M. *IDW '98-The Fifth International Display Workshops*, 1998.
11. Tsuruoka, Y. In: *Proceeding of Electronic Display Forum*; Yokohama, Japan, 1998.
12. Fujii, H.; Tanabe, H.; Harayama, M.; Ota, M. *SID '92 Digest* 1992, 728.
13. Calbo, L. J. *Handbook of Coatings Additives*; Marcel Dekker: New York, 1987; p. 511.