Aqueous alkali-developable Photosensitive Barrier Rib Paste for PDP and Photolithographic Process

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Barrier rib for the plasma display panel (PDP) was made by photolithographic process utilizing photosensitive barrier rib paste. The barrier rib paste was prepared by first dissolving poly(MMA-co-MAA) binder polymer in butyl carbitol(BC) solvent at 15 wt% concentration. To this solution were added a mixture of functional monomers , Irgacure 651 photoinitiator, and barrier rib power and then the whole mixture was dispersed in the three roll mill for 2 hour. The effect of component and concentration of photosensitive barrier rib paste was studied. After optimization of the paste formulation and photolithographic process, barrier rib could be obtained with good resolution up to 110-120 μm height and 80-90 μm width.

INTRODUCTION

Plasma Display Panels (PDP) is a type of flat panel display which has merit of large display area and wide viewing angle suitable for the wall-hanging TV's. In order for the PDP to acquire high luminance, it is necessary that the discharge gas spaces be as wide as possible and the barrier ribs be as thin as possible. Specifically, it is necessary to form barrier ribs which have a large aspect ratio, a narrow width and fully sufficient strength. As means to form barrier ribs in the PDP, various methods such as screen printing and sandblasting are known. However, the screen printing has the disadvantage of poor workability and application to large area PDP. Thus, the feasibility of a photolithographic process has been under study recently.

In this work, photosensitive barrier rib paste was prepared by first dissolving poly(MMA-co-MAA) binder polymer in butyl carbitol(BC) solvent at 15 wt% concentration. To this solution were added a mixture of functional monomers, Irgacure 651 photoinitiator, and barrier rib powder and then the whole mixture was dispersed in the three roll mill for 2 hr. 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) used as multifunctional monomer , butyl carbitol(BC) as solvent, and Irgacure 651 as photosensitizer were purchased from Aldrich Chemical Co. and used as received. Methyl methacrylate (MMA), methyl acrylic acid (MAA), and tetrahydrofuran (THF) were distilled with calcium hydride.2,2'-Azobisisobutyronitrile (AIBN) initiator from Wako Chemical was purified by recrystallization from methanol. Barrier rib powder used in this study has an approximate composition of PbO 60 wt%, SiO2 10.7 wt%, , Al_2O_3 29.0 wt%, and trace (0.3 wt%)amounts of ZrO.

Synthesis of binder polymer. MMA monomer was copolymerized with MAA at various feed ratio. Polymerization was conducted at 15 % of monomers in THF solvent with 2,2'-azobisisobutyronitrile (AIBN) as initiator. The reaction mixture was purged thoroughly with nitrogen gas and then stirred for 24hr at 60°C. The copolymers were recovered by precipitating in hexane, washed and dried under vacuum

Photosensitive brrier rib paste formulation and process.

Photosensitive barrier rib paste was made by dispersing barrier rib powder containing glass frit and aluminium oxide into liquid vehicle composed of poly(MMA-co-MAA) binder polymer, butyl carbitol solvent, multifunctional monomer, and Irgacure 651 photoinitiator using a three roll mill. The viscosity of barrier rib paste was measured with Brookfield viscometer and adjusted to 8,000-15,000 cps by adding BC solvent. The formation of barrier rib by photolithographic process using photosensitive barrier rib is shown in Fig. 1. This process was carrier out in a clean room to avoid dirt contamination during the coating, drying and UV irradiation process. The barrier rib paste was coated on the glass substrate by using a handy coater with 200-400 μm gap. The thickness of dried barrier rib coating was 100-170 μm . The dried barrier rib was exposured to UV (400-800 mJ/cm^2) through a photomask. The optimum exposure time was determined from a series of experiment to yield correct 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 20 psi pressure to give 3.0 ft/minute development rate. The developed barrier rib pannel was dried at 90°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.

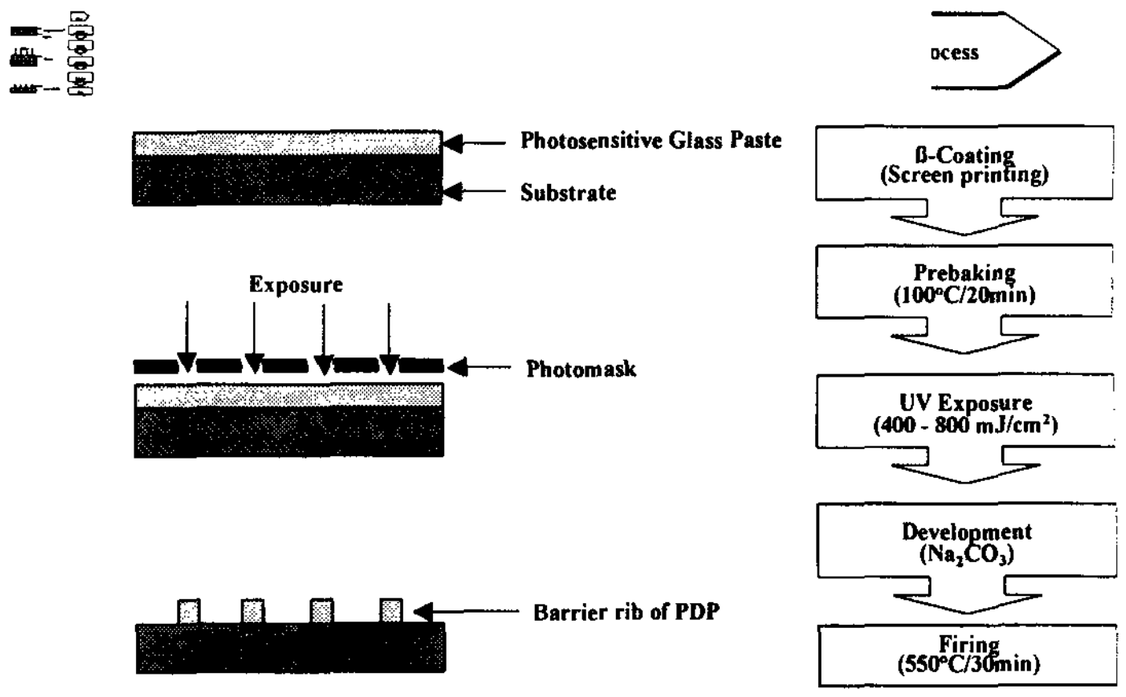


Fig. 1 Formation of PDP barrier rib by photolithographic process.

Measurements. The NMR spectra of poly(MMA-co-MAA) were taken on a Bruker 300 MHz ^{1}H-NMR spectrometer. The

molecular weights of the polymers were obtained by Waters gel permeation chromatograph (GPC) using THF as eluent. Microstructe and barrier rib pattern were examined by SEM.

RESULTS AND DISCUSSION

Synthesis and molecular weight of binder polymer. The structure of binder polymer synthesized is shown in Fig. 2. The molecular weights, composition and yield of copolymers are shown in Table 1. The number average molecular weights of polymer ranged from 10,000 to 190,000g/mol with corresponding polydispersity indices of 1.98-4.45. The copolymer compositions of poly(MMA-co-MAA) samples were nearly same as those of monomer feed.

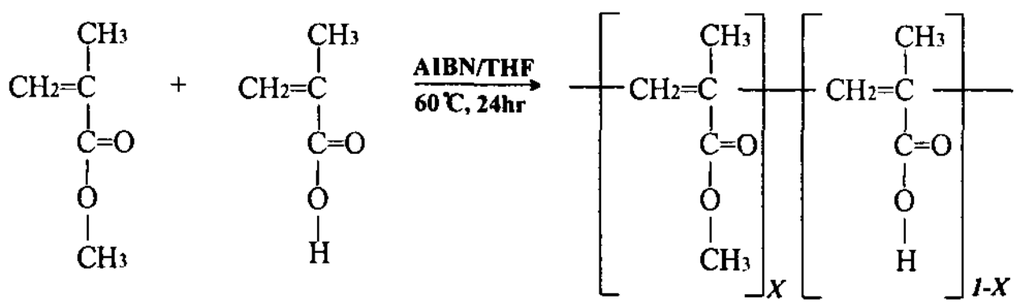
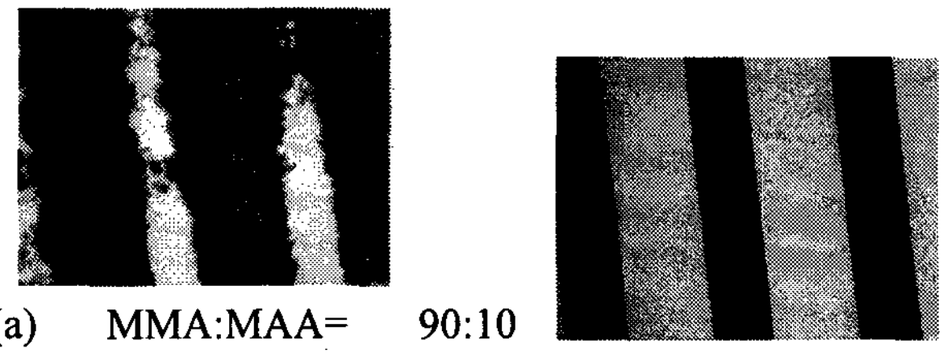


Fig. 2. Structure of poly(MMA-co-MAA).

Table 1. Synthesis and characterization of poly(MMA-co-MAA)

Sample No.	Feed Ratio MMA:MAA (mol%)	Copolymer MMA:MAA (mol%)	Molecular Weight Mw	PDI	Yield (%)
GK-1	90:10	84.3:15.7	21,358	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	20,010	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	70:30	68.5:31.5	19,865	3.60	89.5
GK-7	50:50	53.2:46.8	20,450	4.45	92.5
GK-8	30:70	19.3:70.7	19,985	4.01	93.0

Barrier rib by photolithography Formation of barrier ribs for PDP by photolithographic process depends on both the formulation of photosensitive barrier rib paste and photolithographic process. As for the formulation of photosensitive barrier rib paste, the composition and molecular weight of binder polymer had major effect on the morphology of barrier ribs after development and drying. In Fig. 3 are shown the patterned barrier rib with different binder polymer. Poly(MMA-co-MAA) binder polymer with MMA/MAA=80:20 gave best pattern of barrier ribs. The effect of molecular weight of binder polymer with composition of MMA/MAA=80:20 mole% on the photolithographic process are summarized in Table 2. Binder polymer with MW of about 20,000 g/mole exhibited good barrier rib pattern due to optimum dissolving property in the development stage. The exposure and development time also affected the barrier rib pattern as shown in Fig. 4. Optimum exposure and development time were obtained at 600 mJ/cm^2 and 70 sec, respectively with the optimized photosensitive barrier rib paste. The optimum formulation of photosensitive barrier rib paste was found to be 0.375g poly(MMA-co-MAA), 2.125g BC, 1.5g PETA, 0.3g Irgacure 651 in the vehlcle. The ratio of vehicle to barrier rib powder was about 40:60% by weight.



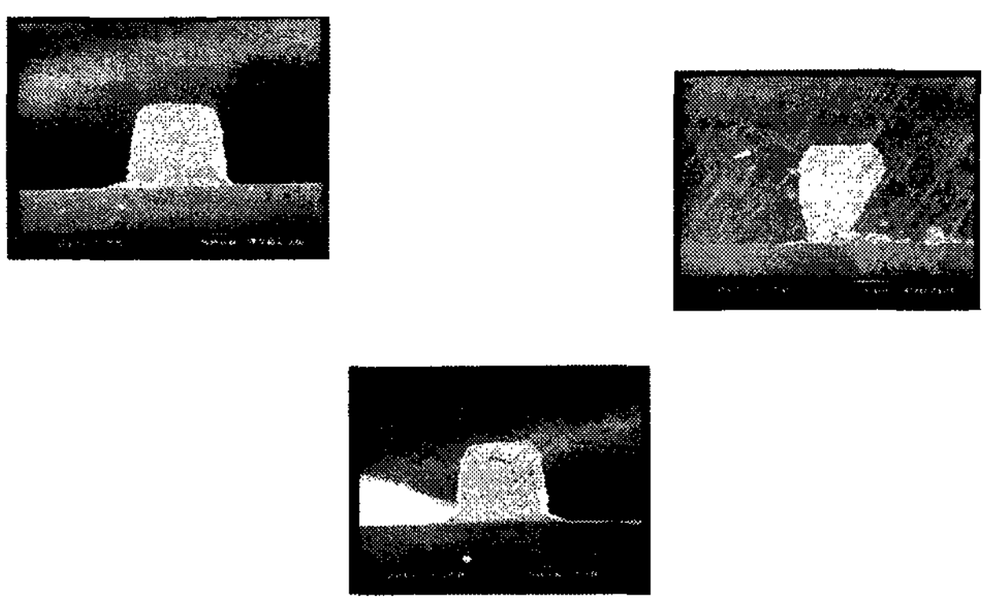
(a) MMA:MAA= 90:10
(b) MMA:MAA = 80:20
(c) MMA:MAA= 50:50
(d) MMA:MAA = 30:70

Fig. 3 Photograph of barrier rib fabricated with different composition of binder polymer poly(MMA-co-MAA)

Table 2 Alkali-developable photosensitive barrier rib paste composition and photolithographic process properties

Device No.	Feed Ratio MMA:MAA (mol%)	Copolymer MMA:MAA (M.W)	Paste (g) Vehicle	Paste (g) Powder	Barrier Rib Pattern
AD-1	90:10	21,358	4.3	6.5	Poor
AD-2	80:20	20,010	4.3	6.5	Good
AD-3	50:50	20,450	4.3	6.5	Poor
AD-4	30:70	19,985	4.3	6.5	Poor
AD-5	80:20	10,900	4.3	6.5	Poor
AD-6	80:20	51,100	4.3	6.5	Poor
AD-7	80:20	190,000	4.3	6.5	Poor

Development Time



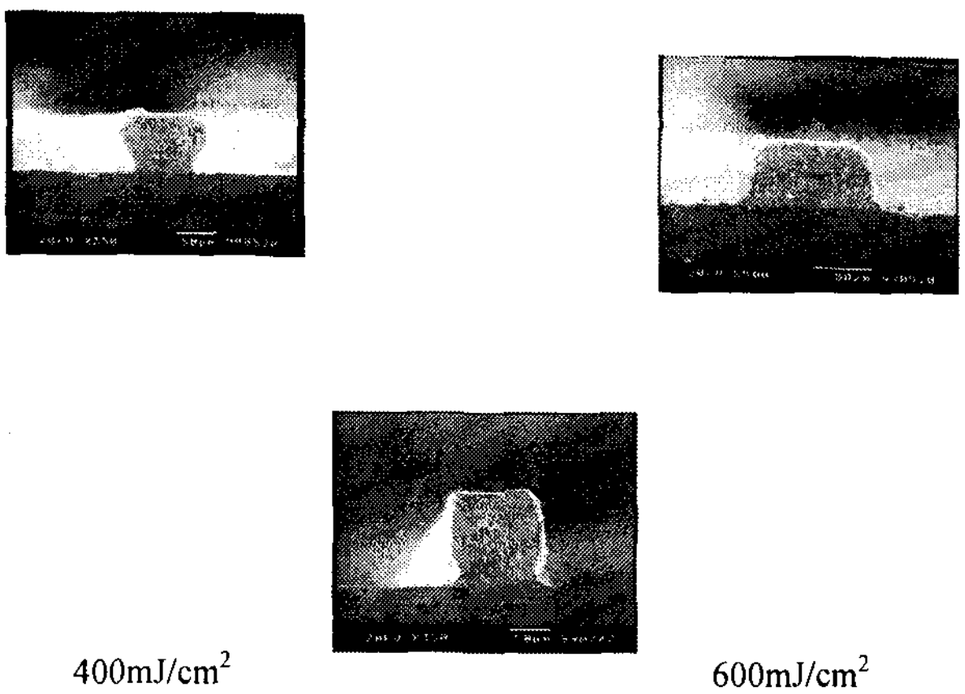


Fig. 4. Effect of exposure and development time on the patterning of barrier rib

CONCLUSIONS

The effect of photosensitive barrier rib formulation and photolithographic process on the patterning of barrier rib for PDP was studied and some important results are as follows;

(1) Poly(MMA-co-MAA)synthesized as binder polymer with MW of about 20,000 g/mol and copolymer composition of MMA/MAA=80:20 mole% exhibited optimum pattern in the photolithographic process of barrier rib formation.

(2) The optimum formulation of photosensitive barrier rib paste was found to be 0.375g poly(MMA-co-MAA), 2.125g BC, 1.5g PETA, 0.3g Irgacure 651 in the vehlcle. The ratio of vehicle to barrier rib powder was about 40:60% by weight.

(3) Optimum exposure and development time were obtained at 600 mJ/cm^2 and 70 sec, respectively with the optimized photosensitive barrier rib paste.

ACKNOWLEDGEMENT

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REFERENCES

[1] Flat Panel Display, PDP Technology, p. 202-207(1997)
[2] Chrstian Decker, Khalil Moussa, Macromol. Chem., Rapid Commun. 11, 159 (1990)
[3] U.S. Patent 5,806,297 (1992)
[4] U.S. Patent 5,703,433 (1997)
[5] Encyclopedia of Polymer Science and Engineering, Wiley-Interscience, 2nd Ed., Vol.3, p226-263(1985)