Effect of Binder Polymer on the Photolithographic Patterning of PDP Barrier Rib

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Keywords: PDP, Barrier Ribs, Photolithography, Binder Polymer, Barrier Rib Paste

Abstract

In this study, the effect of binder polymer on the photolithographic patterning of barrier ribs was studied from view point of polymer structure and barrier rib pattern.

1. Introduction

Barrier ribs in the plasma display panel (PDP) function to maintain the discharge space between the glass plates as well as to prevent optical crosstalk. Patterning of barrier ribs is one of unique processes for making PDP. Barrier ribs could be formed by screen-printing, sand blasting, etching, and photolithographic process.

In the photolithographic patterning of PDP barrier ribs the shape of the barrier rib, especially the depth and width of upper part of barrier are important for the high efficiency PDP panel fabrication

The morphology of the barrier ribs are primarily determined in the exposure and development steps of the photo-process. In the work we synthesized two different types of binder polymers for the photosensitive barrier rib paste and compared their effect on the photolithographic process.

2. Experimental

2.1 Matrials

Pentaerythritol triacrylate (PETA) and bisphenol A epoxy diacrylate (EB 600) were obtained from SK-ucb Company and used as received. Butvl carbitol (BC) as solvent, tyrene(ST), benzyll methacrylate (BMA), and acrylic acid (AA) as monomers were purchased from Aldrich Chemical Company without and used further purification.2,2 -Azobisisobutyronitrile (AIBN) initiator from Wako Chemical was purified by recrystallization from methanol. A mixture photoinitiator (HSP 188) was obtained from SKucb Company and used as received. Barrier rib powder used in the paste has an approximate composition of SiO₂ 40~45 wt %, Al₂O₃ 35~40 wt %, ZnO 5~10 wt %, CaO 5~10 wt %.

2.2 Binder polymers

Two types of binder polymers, poly(St-BMA-AA) and poly(iBMA-MAA-HEMA) were synthesized by free radical copolymerization of Stylene/Butylmethacrylate/Acrylic Acid and Isobutylmethacrylate/Methacylic Acid/2-Hydroxyethylmethacrylate monomers. The characterization of binder polymers are shown in Table I.

Table I. Synthetic Data of Binder Polymers

Sample No.	Feed Ratio	Mw PDI	N _D A.V Cv.
	ST-AA-BMA		
BPA-1	60:30:10	35,500 1.87	1.538 71 89
BPA-2	55:35:10	31,000 1.75	1.536 76 92
BPA-3	45:40:15	33,000 1.82	1.532 81 95
BPA-4	42:43:15	30,515 1.84	1.531 83 96
BPA-5	40:46:14	32,100 1.78	1.525 90 92

Sample No.	Feed Ratio iBMA-MAA(or AA)-HEMA	Mw PDI	N _D A.V Cv.	
BPB-1	50:30:20	9,856 1.88	1.450 121 95	
BPB-2	40:40:20	Gelation		
BPB-3	45:35:20	10,339 1.85	1.448 142 96	
BPB-4	50:(30):20	9,863 1.76	1.445 107 80	
BPB-5	40:(40):20	9,983 1.75	1. 443 126 82	

As shown in Table I. Poly(St-BMA-AA) had higher molecular weight and refractive index than poly(iBMA-MAA-HEMA). However, the acid values were higher in poly(iBMA-MAA-HEMA) series than poly(St-BMA-AA) samples. Fig. 1 shows the polymerization temperature vs. time curves of poly(iBMA-MAA-(orAA)-HEMA) samples.

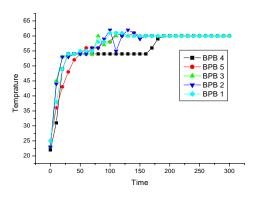


Fig. 1 polymerization temperature vs. time curves

As shown in Fig.1 poly(iBMA-MAA-HEMA) had higher polymerization rate than poly(iBMA-MAA-HEMA) samples. In case of iBMA/MAA/AA=40/40/20 mole%, the polymer was gelled due to too fast reaction rate.

3. Results and discussion

3-1 Barrier Rib paste and pattern

Photosensitive barrier rib paste was made by using the barrier polymers synthesized. First photosensitive vehicle were made mixing binder polymer solution, solvent, UV oligomer and monomer, photosensitizer and photoinitiator.

Photosensitive barrier rib paste was made by dispersing barrier rib powder containing glass frit and aluminum oxide into liquid vehicle composed of binder polymer, solvent, UV crosslinkable monomers, and HSP-188 photoinitiator using a three-roll mill(Exakt 50, Germany). The typical formulation was given in Table II.

Table II. Photosensitive Barrier Rib Formulation

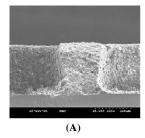
Inorganic powder		Vehicle			Additives
Glass Frit	Filler	PETA	EB- 600	Binder Polymer	PI PS DS
31.2	7.8	3.97	3.97	16.38	2.18 0.2 2.4

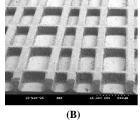
*The weight is shown in grams.PI, PS and DS are photoinitiator, photosensitizer, and dispersant, respectively The viscosity of barrier rib paste was measured with Brookfield viscometer and adjusted to 20,000~29,000 cps range by adding solvent.

The thickness of dried barrier rib coating was varied in the range 180-210 μ m. The dried barrier rib was exposed to UV light (200-800 mJ/cm²) through a photomask. The UV-exposed barrier rib panel was developed with 0.5 wt % sodium carbonate aqueous solution.. The patterned barrier rib was fired in the electric furnace at 550 °C for 30 min to burn out organic materials completely. Microstructure and barrier rib pattern were examined by scanning electron microscopy (SEM). Barrier rib pattern was pretreated with Au deposition, and the acceleration voltage of SEM was 15 Kv.

In the photolithographic method of patterning barrier ribs for PDP, it is desirable to obtain a fine pattern of barrier ribs with one time exposure of UV light. Since the photosensitive barrier rib paste has inorganic powders over 60% weight, these particles scatter UV light during exposure resulting in under-cut in the barrier ribs or washing out of barrier ribs after development.

The shapes of the barrier rib patterns obtained with different binder polymers are shown in Fig. 2. Fine barrier rib patterns with upper and low width of 53 μ m and 84 μ m, and height of 120 μ m would be obtained with the photosensitive paste utilizing poly(iBMA-MAA-HEMA) binder polymer sample BPB-1. However, the paste with poly(St-BMA-AA) as binder polymer could not give barrier rib pattern comparable to those with poly(iBMA-MAA-HEMA) binder polymer.





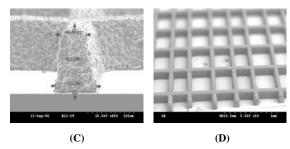


Fig.2 SEM photographs of barrier ribs
(A) BPA4 Cross view, (B) BPA4 Slop view
(C) BPB1 Cross view, (D) BPB1 Slop view

Those results indicated that relatively low molecular weight and refractive index are desirable to get fine pattern of barrier ribs. The low Mw would help uniform dispersion of barrier rib powders in the paste and also contribute to the low viscosity of paste thus resulting in uniform thickness of the barrier ribs. The binder polymer made with monomers containing aromatic rings(i.e. poly (St-BMA-AA)) would also absorb more UV light compared to poly(iBMA-MAA-HEMA) without benzene rings, thus allowing deeper penetration of UV light in the exposure step.

4. Summary

With the optimum design of binder polymer such as molecular weight, acid value and UV light absorption, the photolithographic patterning of barrier ribs could give desirable barrier rib morphology. Thus barrier ribs with upper and lower widths of 53 μ m and 84 μ m and height of 120 μ m could be obtained by using photosensitive barrier rib paste with the optimized binder polymer.

5. References

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