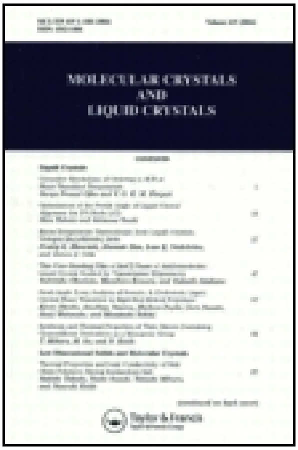

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Photosensitive Paste Formulation and Photolithographic Process for the Fabrication of Barrier Ribs in PDP: Effect of Surface-Treated Fumed Silica

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In this work, formulation of photosensitive pastes was investigated to fabricate barrier ribs of PDP by a photolithographic process. Optimum paste compositions could be achieved by the formulation of alkali-developable polymeric binders, functional monomers, a photoinitiator, and a solvent with barrier rib powders of which surface was treated with fumed silica particles. It was applied to the paste and was found that photolithographic patterns of barrier ribs could be obtained with good resolution up to 110 $\sim$ 120 μm of height and 60 $\sim$ 80 μm of width after sintering. This could be explained by increased light transmittance efficiency through UV light guide channel formed with an aid of nano-sized fumed silica used for surface treatment of barrier rib powders.

Keywords: barrier rib; fumed silica; photolithographic process; photosensitive paste; plasma display panel

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INTRODUCTION

Barrier ribs in plasma display panels (PDPs) function to maintain the discharge space between the glass plates as well as to prevent optical cross-talking. The barrier ribs currently employed are typically $110 \sim 120\,\mu m$ in height, with upper and lower widths of $50\,\mu m$ and $80\,\mu m$, respectively, and $300\,\mu m$ of a pitch. The formation of barrier ribs is one of the unique processes for making PDP and has great effect on the performance of PDP. It has been reported that barrier ribs can be fabricated by screen-printing, sand blasting, etching and photolithographic processes [1–5]. The feasibility of a photolithographic process has been under study recently [6–7]. In the photolithographic process, photosensitive barrier rib paste is coated on the rear glass panel of PDP and then dried. After UV exposure through photo mask 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, resulting in the formation of barrier ribs on the PDP.

In this study, photosensitive barrier rib pastes were formulated and systematically evaluated in terms of photolithographic process variables such as printing, drying, UV exposure, development and sintering. The effect of surface treatment of barrier rib powders with nano-sized fumed silica particles was also studied to improve the resolution of barrier rib pattern by the photolithographic process.

EXPERIMENTAL

Materials

Pentaerythritol triacrylate (PETA) and bisphenol-A epoxy diacrylate (EB 600) were obtained from SK-ucb Co. and used as received. Butyl carbitol (BC) solvent, styrene (ST), benzyl methacrylate (BMA), and acrylic acid (AA) monomers were purchased from Aldrich Chem. Co. and used without further purification. 2,2-Azobisisobutyronitrile (AIBN) initiator from Wako Chemical was purified by recrystallization from methanol. A mixture of photoinitiator (HSP 188) was obtained from SK-ucb Co. and used as received. Approximate composition of barrier rib powder used in the paste was measured to be 60.0 wt% of PbO, 10.7 wt% of SiO_2, 29.0 wt% of Al_2O_3, and trace (0.3 wt%) amounts of ZrO_2.

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(ST-*co*-BMA-*co*-AA) terpolymer binder, BC solvent, UV functional monomers, and HSP-188 photoinitiator using a three-roll mill (Exakt 50, Germany). The viscosity of barrier rib paste was measured with Brookfield viscometer and adjusted to in the range of $20{,}000 \sim 29{,}000$ cps by the addition of BC solvent.

The thickness of dried barrier rib coating was varied in the range of $180 \sim 210\,\mu m$. The dried barrier rib was exposed to UV light ($200 \sim 800\,mJ/cm^2$) through a photo-mask [8]. After UV exposure, the barrier rib panel was developed with 0.5 wt% of 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.

Instrument Analysis

Molecular weights and molecular weight distribution of synthesized polymeric binders were measured by Waters gel permeation chromatograph (GPC) using THF as an eluent. Microstructures of 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.

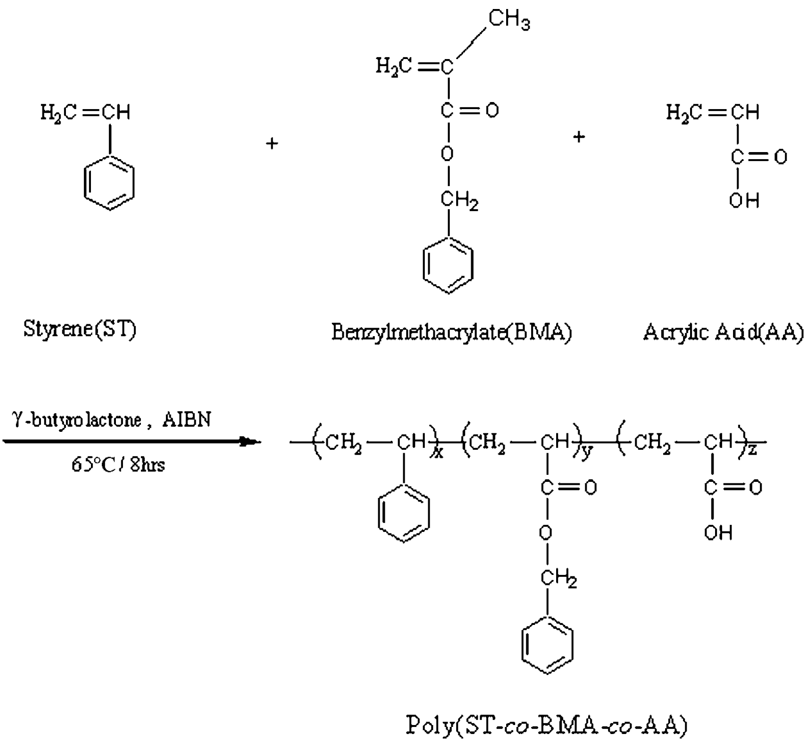
RESULTS AND DISCUSSION

Synthesis of Polymeric Binders for Photosensitive Barrier Rib Paste

Functions of polymeric binders, one of components in photosensitive barrier rib pastes, was known as binding inorganic barrier rib powders, improving the printing quality with thixotropic properties of the pastes during screen printing process, and making the polymeric binder with carboxylic groups in UV-unexposed area developable in alkali solution. Polymeric binders, poly(ST-*co*-BMA-*co*-AA)s, with a variety of compositions were prepared by the free radical polymerization of styrene with N_D (=1.53) similar to that of barrier rib powders, benzyl methacrylate, and acrylic acid with an alkali-developable carboxylic group. The synthetic route to polymeric binders was shown in Scheme 1, and characteristics of synthesized polymeric binders such as molecular weights, polydispersity index (PDI), reflective index (N_D), and acid value were summarized in Table 1.

Effect of the Fumed Silica on UV Transmittance

In the photolithographic method of patterning barrier ribs for PDP, it is desirable to obtain a fine pattern of barrier ribs with one time



SCHEME 1 Synthetic route to the polymeric binder, poly(ST-*co*-BMA-*co*-AA).

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 barrier ribs after development. Therefore, the effect of surface treatment of barrier rib powders with fumed silica on UV transmittance was investigated. In this experiment, barrier rib powders without and with treatment of fumed silicas of 12 nm and 40 nm in

TABLE 1 Characterization of Polymeric Binders, Poly(ST-*co*-AA-*co*-BMA)

Sample no.	Feed ratios ST:AA:BMA	Mw	PDI	N_D	Acid value
BP-1	60:30:10	29,120	1.85	1.538	70
BP-2	55:35:10	31,000	1.91	1.536	76
BP-3	45:40:15	32,000	1.88	1.532	81
BP-4	45:40:15	30,510	1.86	1.531	83
BP-5	40:43:17	33,000	1.88	1.525	90

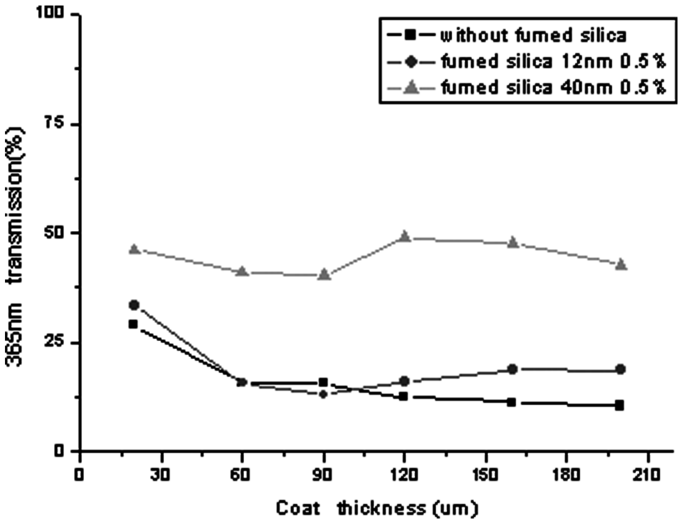


FIGURE 1 Improved transmission in the photolithographic patterning of barrier ribs.

size, respectively, were used in order to compare UV transmittance efficiency on barrier rib layers. It was observed in Figure 1 that the composition using barrier rib powders without surface treatment exhibited low UV transmittance (~20%) due to scattered UV light by barrier rib powders. On the other hand, great improvement of UV transmittance (>40%) was obtained when barrier rib powders were treated with 40 nm of fumed silica. This might be originated from increased light transmittance efficiency through UV light guide channel formed with an aid of fumed silica used for surface treatment of barrier rib powders.

Paste Formulation and Photolithographic Process

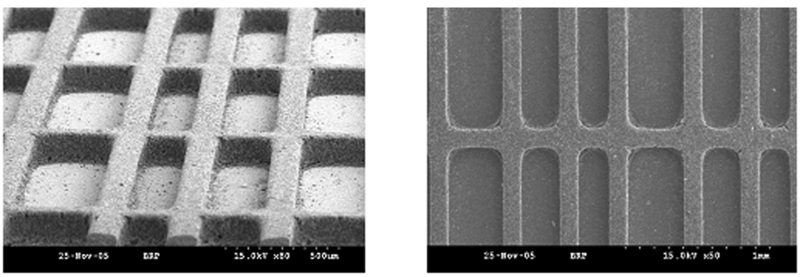
Since the major component of the photosensitive barrier rib pastes, i.e., polymeric binder, was selected, photosensitive vehicles were made with the polymeric binder, a solvent, UV oligomers, a photosensitizer and a photoinitiator [9–11]. Other components in photosensitive vehicles, except the polymeric binder, were previously studied widely in our lab [12–14]. Then photosensitive barrier rib paste was formulated by mixing the photosensitive vehicle and barrier rib powder. As shown in Table 2, formulations of PF-3 and PF-4 gave good pattern formation of barrier ribs with wide range of irradiation doses. The SEM images

TABLE 2 Effect of Polymeric Binders on Pattern Formation of Barrier Ribs by the Photolithographic Process

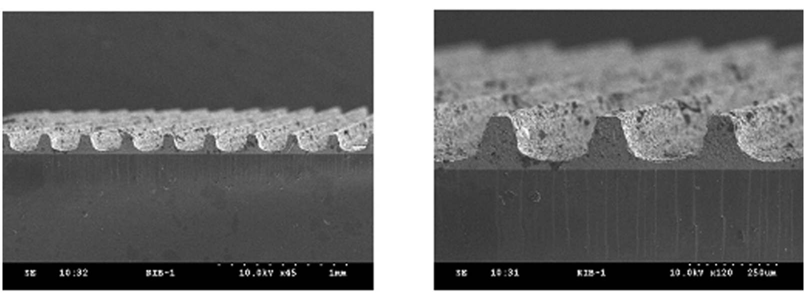
Barrier rib pastes	Polymeric binders	Irradiation dose and pattern shape			
		200 mJ/cm^2	400 mJ/cm^2	600 mJ/cm^2	800 mJ/cm^2
PF-1	BP-1	X	X	X	X
PF-2	BP-2	X	X	X	Δ
PF-3	BP-3	Δ	O	O	O
PF-4	BP-4	Δ	O	O	O
PF-5	BP-5	X	X	X	X

O: Good, Δ: fair, X: bad.

of barrier ribs with 110 ~ 120 μm of height and 60 ~ 80 μm of width obtained with the optimized paste formulation and photolithographic process are shown in Figure 2.



(a) Barrier ribs of well-type structure



(b) Barrier ribs of stripe-type structure

FIGURE 2 SEM photographs of barrier ribs.

CONCLUSIONS

The optimum formulation of photosensitive barrier rib pastes was successfully developed to fabricate barrier ribs of PDP by the photolithographic process. In this formulation, the refractive value of the synthesized polymeric binder, poly(ST-*co*-BMA-*co*-AA) terpolymers, was matched with that of barrier rib powders, and surface treatment of barrier rib powders with nano-sized fumed silica particles was carried out to improve UV transmittance through the light guide channel. As a result, photosensitive barrier rib paste was found to yield a high resolution barrier rib pattern with $110 \sim 120\,\mu m$ of height and $60 \sim 80\,\mu m$ of width by the photolithographic process, followed by sintering process. It can be applied, therefore, as an efficient barrier rib formation process for PDPs, compared to previous sand blasting and etching processes.

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