Material Design for the Fabrication of Barrier Ribs with High Aspect Ratio of Plasma Display Panel by X-ray Lithography

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Abstract

X-ray lithography is one of the most powerful processes in the fabrication of nano/micro structures with a high aspect ratio. This process enables the fabrication of ultra-thin barrier ribs for PDP using X-ray sensitive paste. In this paper, organic material including photo-monomers, photo-oligomers, binder polymer and additives as well as inorganic powders with different size were optimized to fabricate high aspect ratio barrier rib pattern for PDP.

1. Introduction

Several processes are known for the fabrication of barrier ribs for the PDP, such as screen printing [1], sandblasting [2], etching [3], molding [4], and photolithography [5] process. Photolithography process has the problem of chemical waste, but it is easy to align and enables to produce uniform barrier ribs in large area. Therefore it can be adopted in the multi-panel fabrication process for the mass production. However it is not easy to manufacture a slim barrier ribs less than 30 ㎛ in width due to scattering of UV light in an interface between the organic and inorganic material.

The X-ray lithography process is shown in Fig. 1. Studies on X-ray lithography have been preformed to fabricate nano-size patterns for the very large scale integration and high aspect ratio structure (LIGA) using a X-ray resist. Research data on X-ray source, mask, materials and process technologies have been also reported for optimum system and process design. [6,7] We reported on the X-ray lithography by using photosensitive paste for the fabrication of ultra-slim barrier ribs for PDP. [8] In this study, material design in the X-ray lithography was studied in detail for the fabrication of ultra-thin barrier ribs.

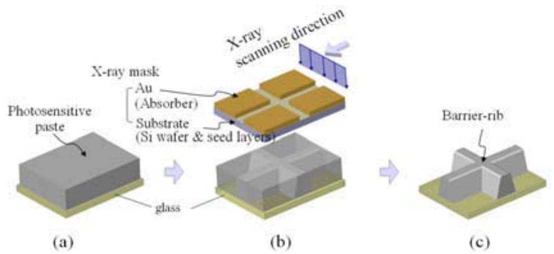

Fig. 1. The X-ray lithography process, (a) coating and drying paste on the substrate, (b) alignment of X-ray mask and X-ray exposure, and (c) development of barrier ribs.

2. Experimental

2.1 X-ray sensitive paste

The X-ray sensitive paste of barrier ribs consisted of inorganic powder and organic vehicle including binder polymers, monomers, oligomers, a photoinitiator, solvent, and additives such as a polymerization inhibitor, a surfactant, and a dispersant. Binder polymers were synthesized by free radical polymerization using iBMA, (M)AA and HEMA monomers. Photo-monomers and photo-oligomers with various functionalities were employed in the vehicle of the paste. A mixed photoinitiator (Irgacure 379, 907) was obtained from Ciba Specialty Chemicals and used as received. The barrier rib powder used in the paste was Pb based inorganic material containing PbO, SiO_2, Al_2O_3, and ZrO_2. The viscosity of the barrier rib paste was about 3,000 ~ 5,000 cPs. The coating thickness of the dried barrier ribs was varied in a range of 180 ~ 200 ㎛.

2.2 X-ray source

X-ray irradiation was carried out with energy of 2.5 GeV and a beam current range of 110 ~ 190 mA using the LIGA beamline (9C1) at the PAL (Pohang Accelerator Laboratory), Korea. Fig. 2 shows a schematic diagram of the LIGA beamline system at PAL. [9]

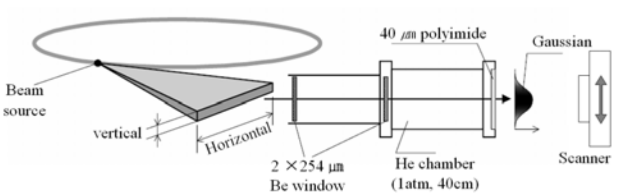

Fig. 2. A schematic diagram of the LIGA beamline system at the PAL.

Some restrictions on the synchrotron radiation are required in order to avoid secondary effects that can influence the quality of the X-ray lithographic patterning of barrier ribs for PDP. In particular, the photon energy range has to be shifted to lower energies to cut the photon flux at substantially higher energies.

3. Results and Discussion

The X-ray sensitive paste was composed of inorganic powder 65 wt% and organic vehicle 35 wt%. The inorganic powder consists of glass frit 80 wt% and alumina filler 20 wt%. Organic vehicle in the paste include binder polymers, monomers, oligomers, a photoinitiator, solvent, and additives such as a polymerization inhibitor, a surfactant, and a dispersant.

Contrary to visible and UV light, high-energy synchrotron radiation is not absorbed selectively by chromophoric groups but absorbed rather unselectively. X-rays of wavelength (λ) between 0.1 and 5 nm interact with shell electrons of atoms in the dried barrier rib layer. The ejected electrons possess enough energy to excite and ionize surrounding atoms or molecules during thermalization. Radical cations and electronically excited molecules generated by excitations or ionizations initiate chemical reactions leading to chemical cross-link in the irradiated barrier rib layer. [10]

The morphology of barrier ribs was affected by diffraction of X-rays, geometric effects and the secondary electron effects. Assuming that organic vehicle only consist of light elements, the size and type of inorganic powder are the important parameters in the X-ray lithography. In this study, three types of barrier rib powder with different size were employed in the paste to identify how these affect the morphology of the barrier ribs by the scattering effects during X-ray exposure step. The average size of inorganic powder were 0.94 ㎛ (type A), 3.03 ㎛ (type B) and 5.51 ㎛ (type C) respectively. The measured data of average powder size (D 50) are shown in Fig. 3.

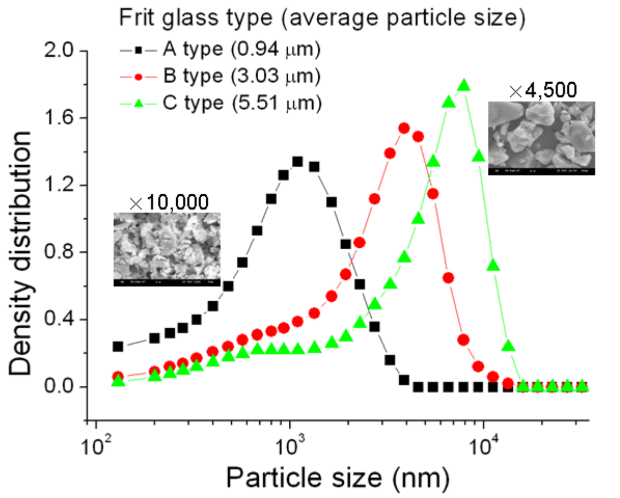

Fig. 3. Density distribution of three types of different frit glass.

The morphology of barrier ribs fabricated by X-ray lithography is shown in Fig. 4. The barrier ribs were fabricated by using X-ray mask with 15 ㎛ in transparent width to X-rays with the barrier rib paste as shown in Fig. 4(a) average size 0.94 ㎛ and (b) size 5.51 ㎛. The barrier ribs paste with sub-㎛ inorganic powder showed undesirable morphology by severe scattering effect as shown in the Fig. 4(a). Scattering problem was not severe in the Fig. 4(b), but the morphology of barrier ribs was not uniform due to too large powder size (type C, 5.51 ㎛) compared to transparent mask width of 15 ㎛ to x-rays

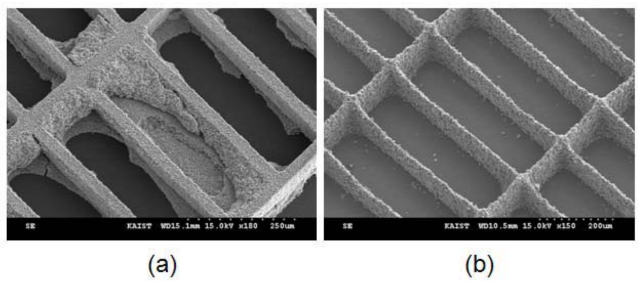

Fig. 4. Barrier ribs fabricated by X-ray lithography using; (a) a powder with average size 0.94 ㎛ (type A), (b) a powder with average size 5.51 ㎛ (type C)

The binder polymer plays an important role in controlling the viscosity of the barrier rib paste. It should also have optimal acid value to fabricate the barrier ribs with desirable morphology during the development step by using aqueous alkaline solution. It was synthesized in the three neck flask with a stirrer and condenser using iBMA-(M)AA-HEMA monomers and a free radical initiator α, α'-azobis(isobutyronitrile) (AIBN). Polymerization was conducted in γ-butylrolactone solvent for 6 hours at 60 ℃ under nitrogen atmosphere. The polymer solution was used directly in the vehicle without purification process.

The synthetic data of the binder polymers are shown in Table 1.

The composition of organic vehicle used in the preparation of X-ray sensitive barrier rib paste is shown in Table 2. A tri-functional monomer pentaerythritol triacrylate (PETA) was used as a photo-monomer and an urethane acrylate UV oligomer (EB600) was used as a photo-oligomer with refractive index of 1.56. The X-ray lithographic patterning of barrier ribs with desirable morphology was obtained by using binder polymer (poly (iBMA-MAA-HEMA) in the feed mole ratio of 5:3:2) with molecular weight (Mw=9,856 g/mol) and acid value (A.V=121).

TABLE 1. Synthetic data of binder polymers

Sam-ple	Formulation	Ratio	A.V	Cv.	Mw
I	iBMA-MAA-HEMA	5:3:2	121	95	9,856
II	iBMA-MAA-HEMA	4:4:2	Gelation		
III	iBMA-MAA-HEMA	4.5:3.5:1	142	96	10,339
IV	iBMA-AA-HEMA	5:3:2	107	80	9,863
V	iBMA-AA-HEMA	4:4:2	126	82	9,983

A.V: Acid Value, Cv. : Conversion, Mw: Molecular Weight.

TABLE 2. Composition of organic vehicle used in the X-ray sensitive barrier rib paste

B.P	P.M	P.O	Solvent	Additive
40 wt%	20 wt%	20 wt%	8 wt%	12 wt%

B.P : Binder polymer, P.M : photo-monomer, P.O : photo-oligomer

X-ray radiation induces a curing reaction with three-dimensional cross-link structure in the dried layer of X-ray sensitive paste. The electromagnetic spectra of the X-ray beam line at PAL uses white light spectral regime to take advantage of the high power density which can generate free radicals easily in the X-ray sensitive paste. The residual content of the C=C double bond in the dried barrier rib layer should be a good parameter to get an optimum X-ray dose. Two types of X-ray sensitive barrier rib pastes were prepared one with a photoinitiator which is usually used in the photolithographic formulation utilizing UV light and the other without. The residual C=C double bond with a wavenumber from 1620 to 1640 was measured by FTIR. The results of the paste without photoinitiator measured are shown in Fig. 5. The X-ray dose leading to optimal formation of precise barrier ribs was 1.56 J/cm^3. There was no significant change in the residual C=C double bonds at the optimal dose condition. However, the residual C=C double bonds in the dried barrier rib layer exposed to an X-ray dose of 12.53MJ/cm^3 was reduced to 46% compared with the initial layer. Polymerization of acrylic resin did not occur in the paste without a photoinitiator in the photolithography process using UV light as energy source. However, polymerization of the acrylic resin did occur in the X-ray lithography due to the high power irradiation which could generate free radicals even without photoinitiator

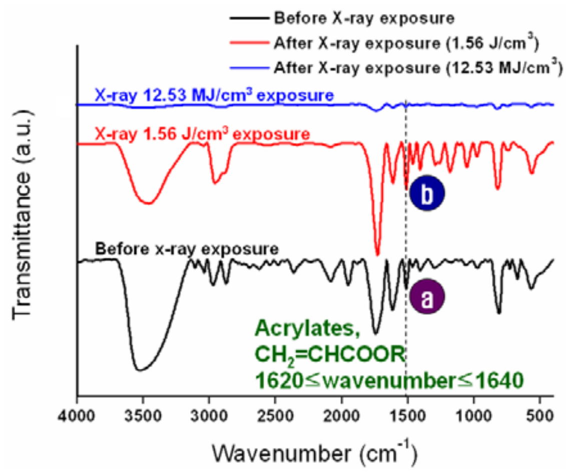

Fig. 5. FTIR analysis of the X-ray lithographic process with a barrier rib layer without a photoinitiator.

SEM images of barrier ribs fabricated by X-ray lithography under optimized X-ray exposure condition with a mask open width of 30 ㎛ are shown in Fig. 6.

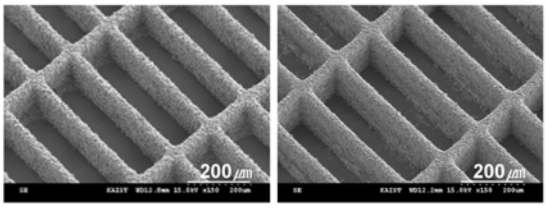

Fig. 6. SEM images of barrier ribs fabricated by X-ray lithography using; (a) a paste without a photoinitiator, (b) a paste with a photoinitiator (0.2 wt%).

A photoinitiator and sensitizer are positive additives to accelerate polymerization of photo-monomers and photo-oligomers. A polymerization inhibitor is negative additive to decelerate polymerization of photoinitiator and photo-oligomer by quenching radicals.

Photoinitiator and polymerization inhibitor were used to control the desirable morphology of barrier ribs, particularly in the cross area of barrier ribs. The images of barrier ribs obtained on the top view are shown in Fig. 7. In the case of paste with inhibitor 0.2 wt% and photoinitiator 0.4 wt% the optimal dose of X-rays was about 783 mJ/cm^3. The contents of photoinitiator and polymerization inhibitor were further reduced to fabricate more desirable morphology of barrier ribs, especially rib width and cross region of ribs. The thin width of barrier ribs and more desirable morphology on the cross region of the ribs could be obtained from the paste without photoinitiator and with polymerization inhibitor 0.5 wt%. The optimal dose of X-ray was 1475 mJ/cm^3. This result was in contrast with the UV photolithography in which leading to three dimensional cross-links could not occur without a photoinitiator.

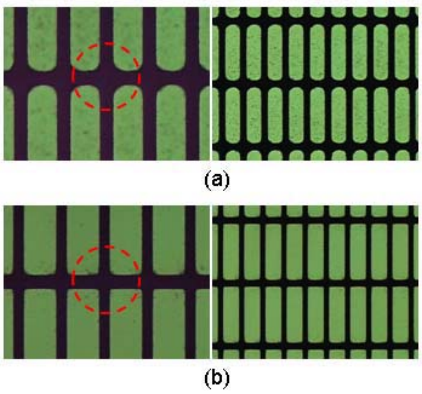

Fig. 7. Top view of barrier ribs made from; (a) inhibitor 0.2 wt% and photoinitiator 0.4 wt%, (b) inhibitor 0.5 wt% and photoinitiator 0 wt%

4. Summary

Some important results of this study were as following. Less scattering phenomenon was observed with X-ray lithography compared to the photolithography using UV light source in the patterning of barrier ribs, especially with inorganic powders with more than 3 μm in the average diameter. Excessive scattering of X-ray was observed in the paste using the inorganic powders with sub-μm size diameter. Optimization of both inorganic and organic materials in the paste was required to reduce scattering problem in the X-ray lithography. Barrier ribs with upper widths of 20 μm and height of 200 μm could be obtained by using X-ray sensitive paste with the optimized binder polymer and additives.

5. Acknowledgements

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6. References

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