P-69: PDP Fabricated with Low-Temperature Processes Below 300°C Using Sol-Gel Hybrid Polymers (Hybrimer PDP)

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Abstract
PDP was fabricated using low-temperature processable sol-gel hybrid polymers (hybrimers) as the dielectric and barrier rib materials replacing the glass frits. All the processes including dielectric coating, barrier rib molding fabrication, phosphor printing and sealing were performed at low temperature below 300°C. This new process is easy, simple and cheap to be capable of producing a large PDP with high yield without applying high temperature processes.

1. Introduction
PDP is fabricated with high-temperature process above 500°C with sintering the glass frits to form the dielectric layer on the front plate, barrier rib on the rear plate, and sealing the front and rear plates in the panel [1]. This high-temperature process using the glass frits gives high fabrication cost and low yield to fabricate the large size panel although PDP has a simple panel structure. Also, the high temperature can deteriorate the phosphor resulting in low efficiency. Thus, the low-temperature process is essential to fabricate the large size PDP with lower cost and higher yield to compete with LCD. It was reported that the silicone resin was used as the materials of dielectric layer and barrier rib as well as sealing to fabricate low electric power consumed PDP [2]. However, it is doubtful to be thermally resistant during plasma discharge. In this study, we used low-temperature (below 200°C) curable sol-gel hybrid polymers (hybrimers) to be more stable than conventional polymers replacing the glass frits to form the dielectric layer and the barrier rib to fabricate PDP. Also, the phosphor paste using low-temperature decomposable binder was prepared to be fired at below 300°C. The PDP test panel was fabricated by sealing the plates using the epoxy sealant which is curable at low-temperature and will be evaluated to demonstrate the feasibility of the hybrimer PDP. Therefore, it will be approved all the fabrication processes were applied at temperature less than 300°C to fabricate the PDP. Also, it is anticipated the fabricated hybrimer PDP will consume low electric power due to low dielectric constant of the hybrimer.

2. Sol-Gel Hybrid Polymers (Hybrimers)
Sol-gel hybrid polymers (hybrimers) are fabricated by thermal- or photo-curing of nano-sized organo-oligosiloxane resins which are synthesized by simple sol-gel reaction of conventional organosilanes. Since condensation of organo-silanes is very sensitive to precursors and reaction scheme, the conditions were optimized to synthesize fully condensed organo-oligosiloxanes [3-5]. The synthesized organo-oligosiloxanes have 2-10 nm sizes composed of several siloxane bonds depending on the precursors and the reaction schemes. The stable hybrimer resin is convenient to be processed for uniform thick coating and simple soft molding. Following polymerization of the organo-oligosiloxane resins by thermal or UV curing results in fabrication of hybrimers as illustrated in Figure 1. Since complete polymerization can make the enhanced characteristics of hybrimers, the composition and curing condition were controlled to promote the polymerization. The final molecular structure of the hybrimer consists of the dispersion of the oligosiloxanes in the polymer matrix (Figure 1) to present high transparency and improved thermal stability compared to the conventional polymers. Mixing of intermediate organic monomers or oligomers with the organo-oligosiloxane resins can increase the polymerization degree. Also, their electrical and optical characteristics can be tuned easily by changing the composition of inorganics and organics. Specially, the fabricated hybrimers have great potential for the application of optics and displays since they are extremely transparent.

![Figure 1 Fabrication of hybrimers using sol-gel synthesized organo-oligosiloxanes](image-url)
Table 1 Characteristics of epoxy-hybrimers for dielectric layer and barrier rib

<table>
<thead>
<tr>
<th></th>
<th>Dielectric Layer</th>
<th>Barrier Rib</th>
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<tbody>
<tr>
<td>Resin</td>
<td>Thermally-curable epoxy-oligosiloxane</td>
<td>Photo-curable epoxy-oligosiloxane + Rutile powder (15 vol %)</td>
</tr>
<tr>
<td>Transparency</td>
<td>&gt;90% (25μm thickness)</td>
<td>-</td>
</tr>
<tr>
<td>Reflectivity</td>
<td>-</td>
<td>&gt;80% (visible)</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.57 (633nm)</td>
<td>-</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>~3.50 (100kHz)</td>
<td>~4.66 (100kHz)</td>
</tr>
<tr>
<td>Breakdown voltage</td>
<td>&gt;3MV/cm</td>
<td>-</td>
</tr>
</tbody>
</table>

3. **Hybrimer Dielectric Layer Coating**

For dielectric layer on the front plate, the epoxy-hybrimer resin was coated using a bar coating method. The coating thickness was controlled by changing the viscosity of the resin adding a solvent. The hybrimer dielectric layer with about 25μm thickness was dense and uniform without any pore as shown in Figure 2. The coating layer was extremely transparent to have over 90% transmission and had higher breakdown voltage over 3MV/cm² enough to insulate electrodes on the substrate. Refractive index and dielectric constant of the coating layer was 1.57 at 633nm and 3.50 at 100kHz, respectively, which can be simply tuned by changing the composition. Dielectric constant of the hybrimer coating layer was much lower than that of glass dielectric layer used in conventional PDP.

![Figure 2 SEM micrograph of hybrimer coating dielectric layer cross-section](image)

4. **Hybrimer Barrier Rib Soft Molding**

Many processes have been used in the fabrication of barrier ribs such as screen printing [1], sand blasting [6], etching [7], molding [8], and photolithography [9] processes. Molding process is the simplest process and has many advantages such as no waste of materials, short process time, and low cost. However, the molding of the glass paste to form large-sized structure is not easy since it requires high pressure to mold the viscous paste. On the other hand, the hybrimer resin can be easily molded like other polymer resins. The photo-curable epoxy-oligosiloxane resin was mixed with 15 vol% filler (TiO₂ rutile powder) to enhance the reflectivity of the barrier rib. Basic characteristics of the hybrimer for the glass rib are represented in Table 1. The reflectivity was over 80% in the visible region and dielectric constant was approximately 4.66 at 100kHz which was also lower than that of glass barrier rib used in conventional PDP. The resin was dispensed onto the rear glass plate and soft-molded using the transparent PDMS mold to form the barrier rib structure. UV-curing of the molded epoxy-hybrimer barrier rib structure made the soft PDMS easily peeled-off. Then, the molded structure was heated at 200°C for sufficient time to harden the structure and remove the organic residues. The finally fabricated barrier rib structure with approximately 125μm height and 70μm width is shown in Figure 3. The size of the molded structure is almost identical with the mold structure due to the low shrinkage of the hybrimer during the curing. Also, the fabricated barrier rib has uniform sizes over the 7.5” rear glass substrate.

![Figure 3 SEM micrographs of hybrimer barrier rib formed by soft molding using a PDMS mold](image)
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5. Low-Temperature Baking Phosphor Paste Printing

We synthesized and adopted the low-temperature burnable P(MMA-co-BMA) random copolymer binder to prepare the low-temperature baking phosphor paste. The phosphor paste was made by adjusting ratio of phosphor: polymer binder: solvent [10]. Figure 4 displays the thermogravimetric and differential thermogravimetric analysis (TGA & DTG) of the vehicle with the P(MMA-co-BMA) binder where temperature is shown in the inset. The binder was completely decomposed by 60min corresponding to about 300°C. Also, it was observed that the binder did not remain without any carbon residue after baking at 300°C. Thus, it was confirmed that the binder was burnable during heating at 300°C and the phosphor paste can be used in the hybrimer PDP.

![Figure 4 TGA/DTG data of vehicle with P(MMA-co-BMA) random copolymer binder](image)

6. Test Panel Fabrication

4” or 7.5” test panels were fabricated on the electrodes patterned plates by the procedure represented in Figure 5. The hybrimer resin was coated using a simple bar coater on the front plate and heated at around 200°C for 1-2 hours in air. On the hybrimer coating dielectric layer whose thickness was approximately 25 μm, MgO protective layer (~500nm thickness) was deposited at 150°C using E-beam evaporation. On the rear plate, the green phosphor paste with Zn2SiO4:Mn2+ and YBO3:Tb3+ mixture phosphor was printed into the rib channels and was fired at 280°C for 1 hour in air. The front and rear plate were sandwiched using an aligner and sealed with an epoxy sealant (Duralco 4703, Cotronics Co.) by curing at 200°C. Then the panel was heated up to 180°C and evacuated to 2x10⁻⁶ Torr. Due to the use of epoxy sealant, the heating temperature was limited. The mixed gas of Ne-4%Xe was filled to the pressure of 450 Torr. Green discharge of the fabricated PDP was made by applying the voltage less than 300V as shown in Figure 6. However, the performance of the fabricated panel was inferior to be evaluated compared to conventional PDP using the glass plates. The fabrication process as well as the materials will be improved to exhibit the feasibility of the hybrimer PDP.

![Figure 5 Schematic procedure for fabrication of hybrimer PDP test panel](image)

![Figure 6 Green discharge of hybrimer PDP test panel](image)

7. Conclusion

Newly developed hybrimer, that is curable at low temperature and is more thermally and chemically stable than polymers, was used as the materials of dielectric layer and barrier rib in the PDP replacing the glass pastes. The hybrimer was coated on the front plate and soft-molded to form barrier rib on the rear plate and cured below 200°C. Then, the MgO was deposited on the hybrimer dielectric layer and the low temperature burnable green phosphor paste was printed on the channel in the barrier rib and fired at 280°C. Green discharge of the test panel fabricated by sealing the plates using the epoxy sealant was demonstrated.
8. Acknowledgements
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9. References


