Polyimide Coatings for OLED Applications

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We developed novel positive-tone photosensitive polyimide coatings for insulation layers in organic light emitting diode (OLED) displays. We evaluated the features of the novel coatings in comparison to other candidate polymers including novolak resin, acrylic resin, and polybenzoxazole. After curing, the novel coatings exhibited excellent and stable electrical and thermal properties, and good adhesion to various substrates with quite a low thickness loss during cleaning process, e.g., UV-O₃, O₂-plasma, etc. In addition we confirmed that the novel coatings could solve the “pixel shrinkage” problem in OLED displays.

Keywords: polyimide, positive-tone photosensitive, OLED, insulation layer, outgas, low tapered angle, pixel shrinkage

1. Introduction

Organic light emitting diode (OLED) displays are promised to be one of the next generation displays due to their various advantages including a wide viewing angle, fast response, low power, and simple structure. OLED displays are composed of an ITO glass, an insulation layer, organic emitting layers (hole-transport layer, emitting layer, electron transport layer, etc.), a cathode layer, and drive units basically (Figure 1).¹ The insulation layer is patterned by photolithographic technology. Requirements for insulation-layer materials are shown as followings. Meeting these requirements results in a solution of a light-emitting problem, “pixel shrinkage”.

- 1) Photosensitivity for a patterning process
- 2) To be curable at less than 250°C
- 3) Round shape and ca. 20-degree tapered-angle at the cross section
- 4) High and stable dielectric strength
- 5) Thermal stability (no outgas)
- 6) Good adhesion to various substrates

Candidate materials for an insulation layer include silicon oxide, silicon nitride, polyimide coatings, novolak photo-resist,^{2,3} acrylic resin, and polybenzoxazole.^{4,5} Among these materials silicon oxide, silicon nitride, or non-photosensitive

polyimide were chosen for an insulation layer in the beginning of the R&D. Furthermore, a positive-tone photosensitive coating, which was composed of a conventional polyimide precursor and a naphthoquinone diazide compound was developed^{6,7}. But it was not able to have a fine patterning due to its poor photosensitivity.

In this article we introduce the novel photosensitive polyimide coatings in comparison to the other polymer candidates from the point of various properties for an OLED insulation layer.

Figure 1. An example for OLED structure

2. Experimental Section

2.1 Materials and synthesis

All compounds and solvents were purchased and provided from chemical manufacturers and

used for experiments without further purification. The following five coatings were prepared.

(1) Polyimide precursor (PI)

19.0g of 4,4'-Diaminodiphenyl ether and 1.2g of bis(3-aminopropyl)tetramethyldisiloxane were dissolved in 300ml of N-methyl-2-pyrrolidone (NMP). 21.8g of pyromellitic dianhydride were added to the NMP solution on a water bath for 1 hour. Then the solution was stirred at 55°C for 4 hours.

A novel polyamic acid coating was prepared by the same procedure with different monomers. A naphthoquinone diazide compound was added to the coating.

In this way we prepared two types of polyimide coatings, which are a non-photosensitive polyimide coating and a novel positive-tone photosensitive polyimide coating.

(2) Novolak photo-resist (novolak PR)

We used "OFPR-800" (Tokyo Ohka Kogyo) as representative of a positive-tone novolak photo-resist.

(3) Acrylic resin

10g of methacrylic acid, 40.0g of *p*-vinylbenzylglycidyl ether, and 3.0g of 2,2'-azobis-2,4-dimethylvaleronitrile were dissolved and polymerized in 100g of diethyleneglycoldimethylether. 15.0g of benzophenone-type naphthoquinone diazide-5-sulfonyl ester was added to the obtained polymer solution.

(4) Polybenzoxazole precursor (PBO)

36.6g of 2,2-Bis(3-amino-4-hydroxyphenyl)-hexafluoro-propane was dissolved in a mixture of N-methyl-2-pyrrolidone 150g and acetone 30g at room temperature, then cooled down to 3°C. 29.5g of glycidyl methyl ether was added to the solution. And 88g of diphenyl ether dicarboxylic acid chloride, which was dissolved in 100g of acetone, was dropwised to the solution with keeping the temperature at 10°C or below. After the dropping, it was stirred at 3 °C for 2 hours, then heated to room temperature. In addition, 3.32g of norbornene-dicarboxylic anhydride was added, then stirred at room temperature for 1 hour.

The solution was poured to 2L of water. Polymer powder was collected by filtration and dried in an oven. 5g of this polymer powder and 2g of benzophenone-type naphthoquinone diazide-5-sulfonyl ester were dissolved in 50g of γ -butyrolactone.

2.2 Pattern profile

Coating solutions were coated on glass wafers (corning 1737) with a spinner to obtain 1.5 μ m thickness. Heat treatment was carried out at 120°C for 2min on a hot plate. Then, the coated wafers were exposed with an i-line stepper (200mJ/cm²; GCA 8570i DSW wafer stepper) and developed by dipping with a tetra-methyl-ammonium hydroxide (TMAH) aqueous solution (2.38wt%) for 30sec. The developed wafers were cured at 230°C for 30min in a convection oven. The pattern profile was evaluated with scanning electron microscopy (SEM; Hitachi S-2300).

2.3 Dielectric breakdown strength stability

Coating solutions were coated on aluminum substrates with a spinner to obtain 2 μ m thickness. Heat treatment was carried out at 120°C for 2min on a hot plate, and 230°C for 30min in a convection oven successively. Dielectric breakdown voltage of the cured film was obtained with a dielectric breakdown voltage measuring equipment (Kikusui electronics TOS9201; JIS C 2110). Dielectric breakdown strength was calculated with dividing the dielectric breakdown voltage by the film thickness.

2.4 Thermal stability (Outgas)

Coating solutions were dropped into aluminum cells which are used for thermal gravimetric analysis (TGA) measurement, and baked under above condition. Thermal weight loss was determined by TGA (Shimadzu TGA-50) with heating from r.t. to 400°C under nitrogen purging.

2.5 Adhesive properties

The coatings were coated on various substrates, e.g., glass, ITO, and SiO₂, and cured under the above condition. Adhesion between cured film and various substrates was determined by a cross cut method (Scotch tape[®] peel test; JIS K 5400) after a pressure-cooker -test (PCT) treatment whose condition is 121°C, 2.0x10⁵Pa (2.0atm), and 100%RH (Espec EHS-211MD).

2.6 O₂-plasma resistance

The coated silicon wafers were prepared under above condition. The film thickness on the wafer was measured after treatment of O₂-plasma cleaning equipment (Iwata Electronic OC-4010) for 5min, 10min, and 20min.

2.7 Solution stability

Viscosity of the coatings was monitored with leaving for 1 month at 23°C (Tokimec TV-20).

2.8 Light emitting performance

An organic electroluminescent device was prepared on an alkaline-free glass substrate of 0.7mm thickness, which had been formed an ITO transparent electrode layer of thickness 130nm. The coatings were patterned on the ITO substrate and baked under above condition. Then it was obtained a structure that ITO edge region was covered with an insulation layer (thickness 1μm) comprising the coatings.

Hole-transport layer and light-emitting layer were formed successively by a vacuum vapor deposition method (2.0×10^{-4} Pa or below). Firstly 50nm of 4,4'-bis[N-(1-naphthyl)-N-phenylamino]-biphenyl (α -NPD) was vapor-deposited over the entire substrate area, then a hole-transport layer was effected. Next 50nm of 8-hydroxyquinoline-aluminum complex (Alq3) was vapor-deposited through a shadow mask, then a patterned light-emitting layer was effected. In addition, aluminum was vapor-deposited through a shadow mask, then a second electrode was effected. In this way, a simple matrix type organic electroluminescent device was prepared.

The device was driven with applying voltage between the ITO electrode and the second aluminum electrode. The emission characteristics were evaluated before and after leaving for 72 hours at 80°C under dry condition. It was observed through a microscope and evaluated "pixel shrinkage" ratio, which means proportion of emitting area in a pixel.

3. Results and Discussion

3.1 Curing temperature

In general, polyimide (PI) or acrylic resin can complete imidization or acrylic polymerization by heating at 200°C. On the other hand polybenzoxazole (PBO) requires higher curing temperature (over 300°C) than the aforementioned polymers for oxazole ring-closing. In addition, although novolak resin showed no change of its polymer structure during heat treatment essentially, it had insufficient heat resistance for the insulation layer as described later.

OLED manufacture requires lower curing temperature than 250°C in order to avoid an influence on work function of ITO. From the point of view of the curing temperature, PI, acrylic resin, or novolak resin are acceptable.

3.2 Patterning properties

Patterning process examples for 1μm film thickness after curing are shown in the Table 1. The patterning method includes spin coating, pre-baking, exposure, development, and curing. The process is similar to a conventional positive-tone photo-resist patterning process.

All coatings except for the non-photosensitive PI were patterned under the condition in Table 1 successfully. But non-photosensitive PI was not able to have a fine patterning due to its non-photosensitivity.

The novel PI can be used with an existing LCD production line, which is composed of a coater, hot plates, a stepper (an aligner), and a developer.

Table 1. Patterning process conditions for thickness 1μm after curing

	(a) Novel PI	(b) Non-photosensitive PI ⁵⁾	(c) Novolak PR	(d) Acrylic resin	(e) PBO
Spin coating	1200 rpm/30s	-	1200 rpm/30s	1200 rpm/30s	1200 rpm/30s
Pre-baking ¹⁾	120°C/120s	-	120°C/120s	90°C/120s	120°C/120s
Exposure ²⁾	200mJ/cm ²	-	200mJ/cm ²	200mJ/cm ²	200mJ/cm ²
Development ³⁾	20s	-	20s	20s	20s
Curing ⁴⁾	230°C/30min	-	230°C/30min	230°C/30min	320°C/30min

1) on a hot plate, 2) i-line stepper, 3) dipping in 2.38% TMAH for 30min and DI Rinse for 30min,

4) in a convection oven, 5) It was not able to have a fine patterning in itself due to its non-photosensitivity.

3.3 Cross sectional views

A shape at the pattern edge of an insulation layer is important for OLED displays. A rectangle shape causes some electrical problems, e.g., electrical short, electric breakdown, and leakage current, etc. For this reason a round shape is suitable for the OLED insulation layer.

Photo 1 and 2 show cross sectional views of 5 μ m and 30 μ m line and space (L&S) for the novel PI. The obtained patterns are enough fine for the insulation layer. In addition, they show round shape and look suitable for an insulation layer. The lower tapered angle at the pattern edge, 20 degrees, is also proper for an insulation layer. We can control the edge from 10 degrees to 60 degrees by changing its formulation.

For the other coatings, novolak PR and acrylic resin also showed round shape and low tapered angle (20 degrees for OFPR-800, 30 degrees for acrylic resin). But the PBO showed rectangle shape and higher tapered angle, 50 degrees (Photo 3).

Photo 1. Cross sectional view of the novel PI 5 μ m L&S, 1 μ m thickness after curing (x10k)

Photo 2. Cross sectional view of the novel PI 30 μ m L&S, 1 μ m thickness after curing (x10k)

Photo 3. Cross sectional view of the PBO 30 μ m L&S, 1 μ m thickness after curing (x10k)

3.4 Dielectric breakdown strength stability

An insulation layer requires the high and stable insulating property, which is exemplified by dielectric strength under severe conditions. Figure 2 shows thermal stability of dielectric strength for the novel PI after curing in a comparison to the other coatings. The novel PI and the non-photosensitive PI showed high dielectric strength 350kV/mm and no damage in 20 days at 85 $^{\circ}$ C, while the acrylic resin and the PBO showed 300kV/mm and 280kV/mm respectively and no damage. The novolak PR showed 200kV/mm and 85% damage.

Figure 3 shows light stability of dielectric strength after curing. The novel PI, the non-photosensitive PI, acrylic resin, and the PBO also had no damage in 20 days irradiation, while the novolak PR had 40% loss in 20 days (Figure 3). These figures prove that PI has the highest and stable electrical reliability on daily use.

Figure 2. Thermal stability of dielectric breakdown strength; (a)novel PI, (b)non-photosensitive PI, (c)novolak PR, (d)acrylic resin, (e)PBO

Figure 3. Light stability of dielectric breakdown strength; (a)novel PI, (b)non-photosensitive PI, (c)novolak PR, (d)acrylic resin, (e)PBO

3.5 Outgas

An insulation layer requires no outgas due to contact directly with OLED emitting materials in a pixel. Outgas is thought to be a major reason for "pixel shrinkage", which is one of the serious problems for OLED displays. On this account lower outgas is desirable. Outgas can be estimated at weight loss by TGA analysis. Figure 4-1 and 4-2 show a comparison of normalized weight loss with heating from r.t. to 400°C.

The novel PI and the non-photosensitive PI showed no weight loss from r.t. to ca.280°C and 10% weight loss at 400°C. The acrylic resin showed 30% weight loss at 400°C. The novolak PR showed weight loss initially and 5% weight loss at 280°C (Figure 4-1). The PBO looks like higher thermal stability because its curing temperature is higher than the other coatings. But the novel PI represents the same weight loss curve as the PBO after curing at the same temperature, 320°C (Figure 4-2).

These mean that PI has higher thermal stability and less influence on OLED emitting materials.

3.6 Adhesive properties

An insulation layer also requires good adhesion to various substrates in order to avoid electrical short at an insulation-layer pattern edge.

Table 2 shows adhesive retention time of the coatings against PCT treatment. Adhesive

Figure 4-1. Thermal gravimetric analysis (1); (a)novel PI, (b)non-photosensitive PI, (c)novolak PR, (d)acrylic resin
Curing: 230°C for 30min in a convection oven

Figure 4-2. Thermal gravimetric analysis (2); (a)novel PI, (e)PBO

Curing: 320°C for 30min in a convection oven

retention time means the first time when the cross-cut film is peeled off even though it is small portion of area. The both of PI coatings showed good adhesion to various substrates after over 500 hours PCT treatment, while the other coatings after curing were peeled off in 50-200 hours PCT-treatment.

This result means that PI has enough adhesion to apply to OLED displays.

3.7 O₂-plasma resistance

O₂-plasma resistance of an insulation layer is important for some cleaning processes before vacuum evaporation process. An insulation layer is affected and slightly removed by O₂-plasma cleaning, which is used for removing contaminations on an ITO pixel.

Table 2. Adhesive retention time* against PCT** treatment

Substrate	(a) Novel PI	(b) non-photosensitive PI	(c) Novolak PR	(d) Acrylic resin	(e) PBO
Glass***	> 500h	> 500h	50h	100h	100h
ITO	> 500h	> 500h	100h	50h	500h
SiO ₂	> 500h	> 500h	50h	200h	100h

Curing: 230°C for 30min in a convection oven [(a), (b), (c), (d)]; 320°C for 30min in a convection oven [(e)]

*Adhesive retention time means the first time when the cross-cut film is peeled off partially, where the longer the time is, the better adhesion is.

**PCT condition: 121°C, 2.0×10^5 Pa (2.0atm), and 100%RH

*** non-alkaline glass #1737 (corning)

Figure 5-1 and 5-2 represent O₂-plasma resistance of the cured films. With O₂-plasma treatment in 20min, the novolak PR showed 7 times thickness reducing rate of the other coatings (Figure 5-1). In addition, PI has the lower reducing rate than the PBO (Figure 5-2). These results are derived from lower oxidation resistance of PBO comparing to that of PI.

The above results mean that PI can be applied to a substrate cleaning process preferably.

Figure 5-1. O₂-plasma resistance of cured films
Curing: 230°C for 30min in a convection oven

3.8 Solution stability

Solution stability of the coatings is important for a mass production process. Solution viscosity has an influence on a coating thickness. Viscosity change of the coatings at room temperature (23°C) is exhibited in Figure 6. The viscosity of the novel PI and novolak PR had a slight change even after a month, which is negligible for the coated

Figure 5-2. O₂-plasma resistance of cured films
Curing: 230°C for 30min in a convection oven [(a), (b)],
320°C for 30min in a convection oven [(c)]

Figure 6. Viscosity stability

	(a) Novel PI	(c) Novolak PR	(d) Acrylic resin
Initial
72h
Pixel shrinkage ratio*	0%	64%	47%

Figure 7. Durability test of light emitting performance

Test condition: 80°C under dry condition

*Pixel shrinkage ratio = light emitting area / pixel area $\times 100$

film thickness. But the acrylic resin showed poor viscosity stability, which is increased from 30 mPa s to 52 mPa s.

3.9 Light emitting performance

Figure 7 shows light emitting durability of OLED panels, which has insulation layers of the coatings. The novel PI showed no "pixel shrinkage" after 72 hours durability test. But novolak PR and

acrylic resin represents 64% shrinkage and 47% shrinkage respectively.

This means that OLED panels with the novel PI have good light-emitting reliability.

4. Conclusion

We developed the novel positive-tone photosensitive polyimide coatings. The coatings have high reliability as well as good photolithographic performance with lower temperature curing nature. The coatings have high and stable electrical properties, excellent thermal stability (no outgas), good O₂-plasma resistance, and good solution stability. In addition, the OLED panel with the coatings as an insulation layer shows excellent light emitting performance (no pixel shrinkage).

These features promise that the novel PI is much suitable for an insulation layer in OLED displays.

References

- 1 H.Nakada and T.Thoma, *Inorganic and Organic Electroluminescence*, EL96, Berlin, 385(1996)
- 2 USP-4093461
- 3 S. L-C. Hsu et al., *J. Appl. Polym. Sci.*, **86**, 352 (2002)
- 4 USP-4332883
- 5 K. Yamamoto and T. Hirano, *J. Photo. Polym. Sci. and Technol.*, **15**, 173 (2002)
- 6 K. Takano et al., *J. Applied Polym. Sci.*, **46**, 1137 (1992)
- 7 S. Hayase et al., *Polym. Adv. Tech.*, **4**(4), 302 (1993)