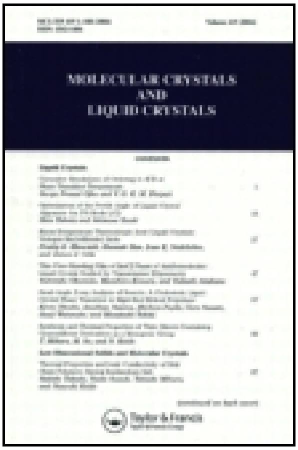

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Synthesis of Imide UV Monomers for Application to Interdielectric Layer of TFT-LCD Array

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Novel negative-type photocurable imide UV monomers were synthesized and characterized for an application to interdielectric layer in TFT-LCD array. Two different imide-type UV monomers were synthesized through 2 step reaction. In addition, alkali developable polymer matrix was also prepared by free radical

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random copolymerization of benzylmethacrylate and methacrylic acid in THF at 65°C. It was found from photolithographic process that via-hole with good resolution were obtained using optimum formulations, suitable for spin coating process, of negative-type imide UV monomers, photoinitiator, UV oligomer, and alkali developable polymer matrix.

Keywords: interdielectric layer; negative-type imide UV monomer; photolithographic process; TFT-LCD

INTRODUCTION

Thin film transistor (TFT) is a switching device consisting of source and drain electrodes, gate electrode, interdielectric layer, and so on. The requirements for the interdielectric layer are relatively high dielectric constant, heat and chemical resistance, photosensitivity, and pinhole free thin film formability with high breakdown voltage and long-term stability. Previously, thermally curable-type benzocyclobutane (BCB) has been used. However, the process using BCB has suffered from low productivity and resolution, and some limitations for dry etch process. Therefore, it is required to design and synthesize new interdielectric layers with high resolution, simple fabrication process by a photolithographic process.

In this article, we report synthesis, characterization, and formulation of negative-type photocurable imide UV monomers for an application as an interdielectric layer in TFT-LCD. Characteristics of photolithographic process using this type of formulation are presented [1,2].

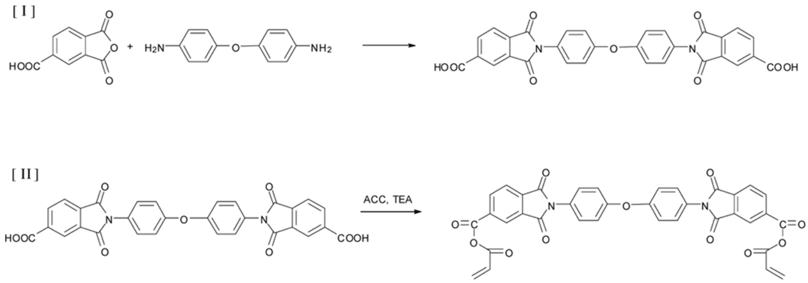
EXPERIMENTAL

Materials

Trimellitic anhydride, 4,4′-diaminodiphenyl ether, 2,2′-bis(3-amino-4-hydroxyphenyl) hexa fluoro propane (Bis-APAF), acryloyl chloride (ACC), triethylamine (TEA), *m*-cresol, benzylmethacrylate, methacrylic acid were purchased from Aldrich Chemical Company. All other chemicals were reagent grades and used as received.

Synthesis of Imide UV Monomer Type-1

The synthetic procedure is presented in Scheme 1. In the first step, trimellitic anhydride was added into *m*-cresol, and stirred at 150°C for 30 min, and then 4,4′ -diaminodiphenyl ether was slowly added into trimellitic anhydride dissolved in *m*-cresol and stirred at 150°C for 6 hrs. Imide UV monomer precursor was obtained by washing with

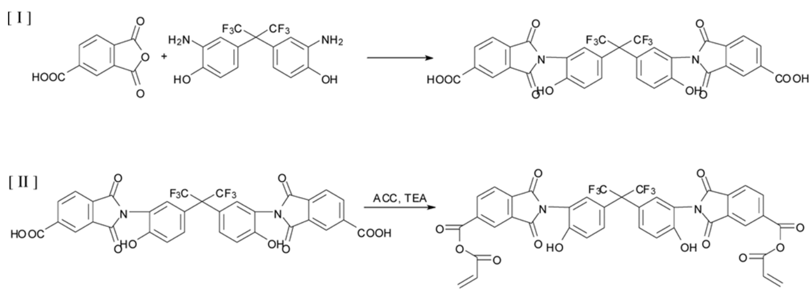


SCHEME 1 Synthesis of imide UV monomer type-1.

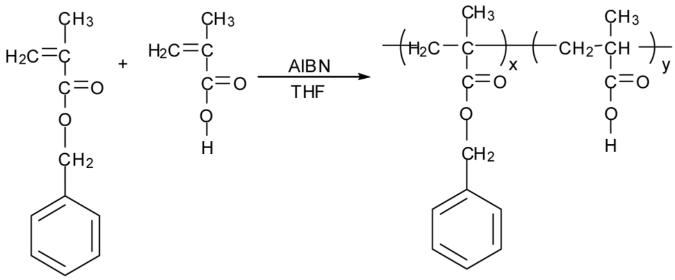
water, filtration and dry process. In the second step, the imide UV monomer precursor, acryloyl chloride (ACC) were dissolved in NMP, and then triethylamine (TEA) was added slowly into imide UV monomer dissolved in NMP and stirred at room temperature for 2 hrs. After reaction was done, TEA and hydrochloride were removed by filtration, and then imide UV monomer type-1 was obtained by precipitation by 1% HCl, filtration and dry process. *FT-IR* (*v in* cm^{-1}): 912 (*aromatic imides*), 713 (=CH) [3–5].

Synthesis of Imide UV Monomer Type-2

The synthetic procedure is presented in Scheme 2. Imide UV monomer type-2 was prepared in the same way for imide UV monomer typy-1. *FT-IR* (*v in* cm^{-1}): 915 (*aromatic imides*), 708 (=CH).



SCHEME 2 Synthesis of imide UV monomer type-2.



SCHEME 3 Polymerization of alkali developable polymer matrix.

Synthesis of Alkali Developable Polymer Matrix

The reaction procedure is presented in Scheme 3. Benzylmethacrylate (58.89 g, 0.334 mol), methacrylic acid (12.32 g, 0.143 mol) were dissolved in THF (280 ml), and stirred at 65°C for 30 min, and then AIBN (1.57 g, 0.01 mol) was added slowly into monomer solution and stirred at 65°C for 6 hrs. Alkali developable polymer matrix was obtained by precipitation by n-hexane, filtration and dry. *FT-IR* (*v in* cm^{-1}): 1798 (C=O *st*, *carbonic acid*), 1178 (C–O *st carbonic acid*).

Photolithographic Process

Photosensitive formulation was spin-coated on ITO-coated glass, followed by soft baking at 120°C for 3 min. The dried film was exposed to UV light (200 mJ/m^2) through a photomask. After UV exposure, the film was developed with 2.38% of TMAH solution. The patterned images were examined by scanning electron microscopy (Hitachi S-570).

RESULTS AND DISCUSSIONS

Pattern Formation by Photolithographic Process

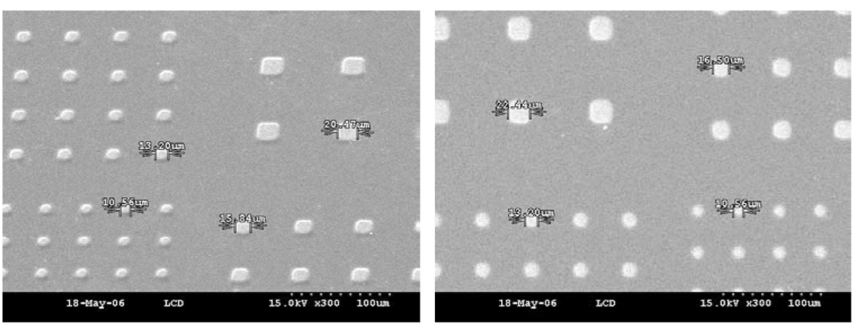
Optimum composition for negative-type photocurable polyimide solution for interdielectric layer of TFT LCD array was formulated with photo initiator (HSP188), photo monomer (Imide UV monomer type-1, type-2), photo oligomer (EB-600), polymeric binder (alkali developable polymer matrix), as shown in Table 1. As can be seen in Figure 1, these compositions were found to yield hole-type polyimide patterns, which size reaches about 10 μm × 10 μm with good resolution through the photolithographic process [6].

TABLE 1 Formulation for Interdielectric Layer

	Type-1		Type-2	
Photo Initiator (HSP-188)	0.065 g	1.30 wt%	0.065 g	1.30 wt%
Photo Monomer (Imide Monomer)	0.325 g	6.50 wt%	0.325 g	6.50 wt%
Photo Oligomer (EB-600)	0.325 g	6.50 wt%	0.325 g	6.50 wt%
Binder Polymer (Poly(BzMA-co-MAA)	0.795 g	15.87 wt%	0.795 g	15.87 wt%
Solvent (DMF)	3.49 g	69.83 wt%	3.49 g	69.83 wt%
Total	5 g	100.00 wt%	5 g	100.00 wt%

Transmittance of Interdielectric Layer After Photolithographic Process

Higher transmittance is required for the interdielectric layer of TFT-LCD array due to its large coverage on the array. However, the application of polyimide films for the interdielectric layer of TFT-LCD array was hampered by its yellowing properties. In this study, a new type of imide UV monomer type-2 was designed and synthesized in order to improve the transmittance property by introducing fluoro (CF_3) groups in the monomer backbone. As presented in Figure 2, the formulation with imide UV monomer type-2 having fluoro group improved the transmittance, showing over 90% of transmittance in 380 nm of blue range, compared to 60% of transmittance from the formulation with imide UV monomer type-1. The result of improved transmittance by employing imide UV monomer type-2 was found to be comparable



(a) (b)

FIGURE 1 SEM photographs of patterned images; (a) using Type-1 monomer and (b) using Type-2 monomer.

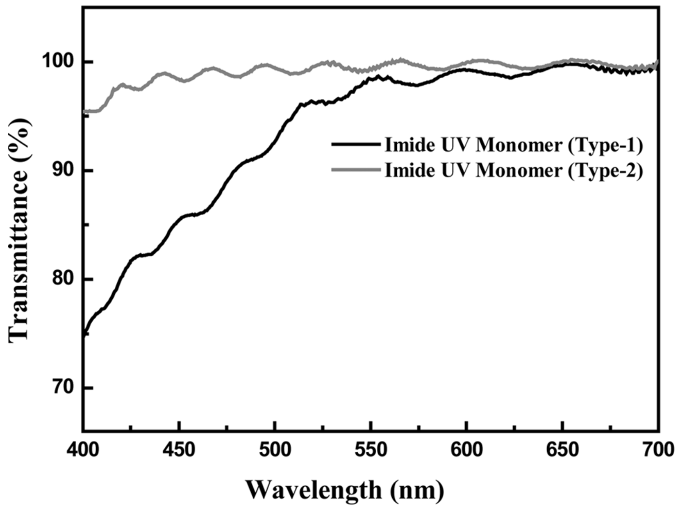


FIGURE 2 Transmittance spectra of Interdielectric layer thin-film using Imide UV monomer Type-1 and Type-2.

to that of conventional thermosetting BCB interdielectric layer of TFT-LCD array [7].

Thermal Property of Interdielectric Layer After Photolithographic Process

It has been known that the temperature for ITO deposition process over the interdielectric layer of TFT-LCD array is above 300°C. Therefore, it is required for the interdielectric layer thin films to have higher thermal property in order to prevent any deformation of the thin films during ITO deposition process. Thermal stability of the conventional interdielectric BCB material was reported to be $365 \sim 475$°C [7]. Figure 3 revealed that thermal degradation of interdielectric layer thin films using imide UV mononers was observed above 400°C, satisfying the required thermal property of the interdielectric layer thin film during ITO deposition process.

CONCLUSIONS

Two different types of imide UV monomers, type-1 and type-2, were successfully synthesized and characterized. Formulations consisting of negative-type imide UV monomers, photoinitiator, UV oligomer,

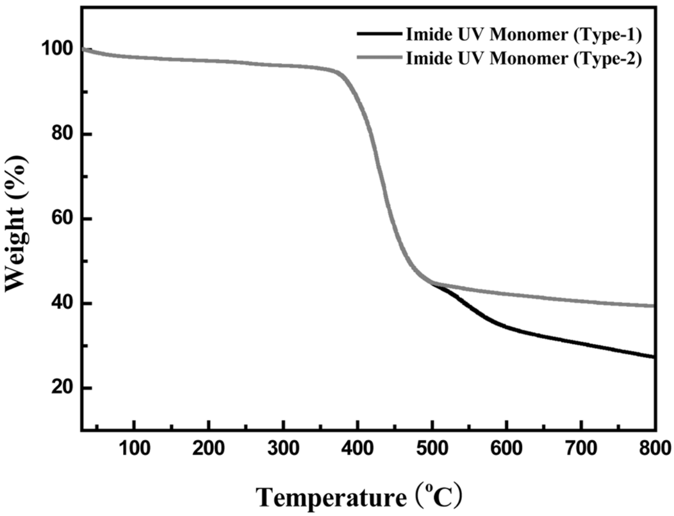


FIGURE 3 TGA characteristics of Interdielectric layer thin-film using Imide UV monomer Type-1 and Type-2.

and alkali developable polymer matrix were optimized for photolithographic process. Pinhole pattern with good resolution ($10 \times 10\,\mu m$) was achieved using the optimized formulations. Moreover, formulation with imide UV monomer type-2 having fluoro group exhibited over 90% of transmittance. In addition, thermal degradation of interdielectric layer thin films using imide UV mononers was observed above 400℃, satisfying the required thermal property of the interdielectric layer thin film during ITO deposition process.

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