Synthesis of Imide Monomers for Application to Organic Photosensitive Interdielectric Layer

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Abstract

A negative photoresist formulation was developed utilizing synthesized UV monomers containing imide linkage, photoinitiator, UV oligomer, and alkali developable polymer matrix. It was found that via-holes with good resolution, high transmittance and thermal resistance could be obtained by photolithographic process utilizing the negative-type photoresist formulations.

1. Introduction

Thin film transitor (TFT) is a switching device consisting of source and drain electrodes, gate electrode, interdielectric layer, and active semiconductor layer. The requirements for the interdielectric layer include relatively high dielectric constant, heat and chemical resistance, photosensitivity, pinhole free thin film forming property, high breakdown voltage and long-term stability. Previously thermally curable formulation containing benzocyclobutane (BCB) has been used. However, the process using BCB has suffered from low productivity, limited resolution, and long bleaching step after photopatterning of interdielectric layers. Therefore, it is required to develop a new interdielectric material with high resolution and simple fabrication by a photolithographic process

In this paper, we report synthesis of imide UV monomers and negative-type photoresist for an application to interdielectric layer in TFT array [1, 2].

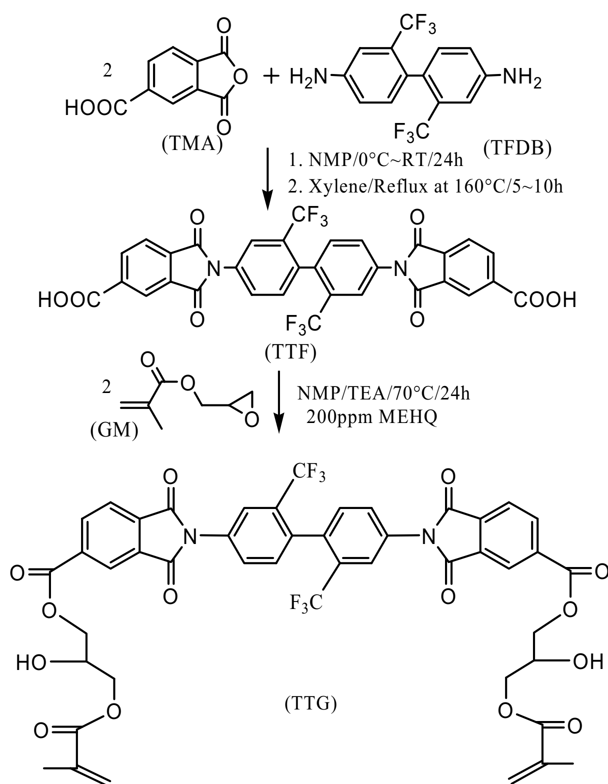
2. Experimental

2.1 Materials

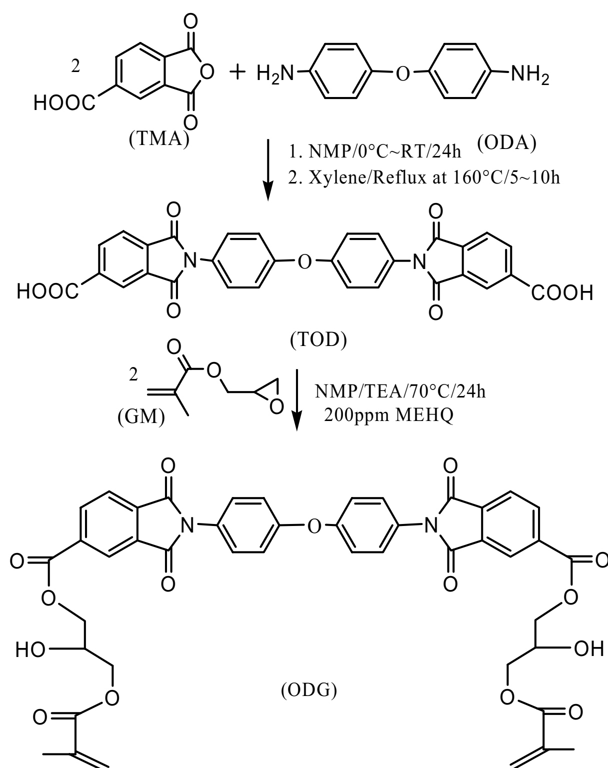
Trimellitic anhydride (TMA), phthalic anhydride (PA), 4,4-diaminodiphenyl ether (ODA), acryloyl chloride (ACC), glycidyl methacrylate (GM), 2,2'–bis(trifluoromethyl) benzidine (TFDB), 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (AH6FP), triethylamine (TEA), 4-methoxyphenol (MEHQ), m-cresol, benzylmethacrylate and methacrylate were obtained from Aldrich Chemical Company and Tokyo Chemical Industry Co., Ltd. All other chemicals were reagent grades and used as received.

2.2 Synthesis of UV Monomers with Imide Core

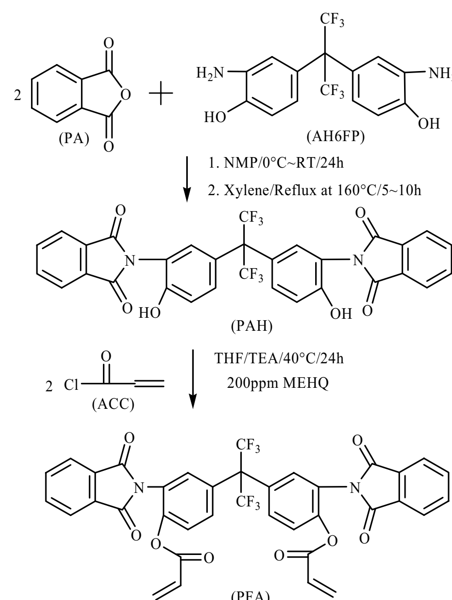
A list of novel imide monomers was synthesized via two-step process. All reactions were carried out in 250ml three-neck round bottomed flask equipped with nitrogen inlet and outlet and a magnetic stirrer. First, we synthesized precursors based on diamines and anhydrides. These reactions were carried out in NMP solvent at ambient temperature for 24h. After adding xylene, reaction mixture was refluxed at 160ºC for at least 5h. Precursors were obtained by precipitation in mixed solvent of water and 0.1N hydroxide chloride (v/v: 90/10), and drying in vacuum oven for 24h. In the second step, we used TEA and MEHQ 200ppm as a catalyst and an inhibitor respectively for synthesis of novel UV monomers containing imide core. TTF and TOD precursors and GM were reacted in NMP solvent at 70ºC for 24h. The UV monomers (TTG and ODG) were obtained by precipitation in mixed solution of water and 0.1N hydroxide chloride (v/v: 90/10), and drying in vacuum oven for 24h. After reaction, THF solvent was removed by rotary evaporator and the product was collected by re-crystallization in ethanol for 48h [3-5]. The reaction procedures are shown in Scheme 1, 2 and 3 and product yields are shown in Table 1.



Scheme 1. Synthesis of UV monomer (TTG)



Scheme 2. Synthesis of UV monomer (ODG)



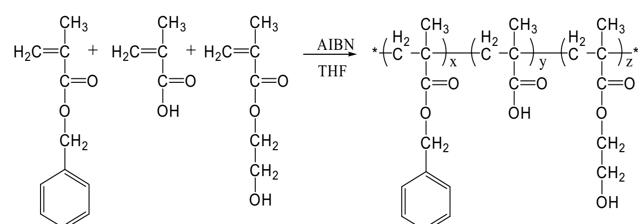
Scheme 3. Synthesis of UV monomer (PFA)

TABLE 1. Yield of precursors and imide monomers

No	Reaction	Yield (%)
1	TTF (TMA+TFDB)	94
2	TTG (TTF+GM)	81
3	TOD (TMA+ODA)	93
4	ODG (TOD+GM)	78
5	PAH (PA+AH6FP)	94
6	PFA (PAH+ACC)	65

2.3 Synthesis of Alkali Developable Binder Polymers

The reaction procedure is presented in Scheme 4. Benzylmethacrylate, methacrylic acid and other monomer combination as shown in Table 2 were dissolved in THF solvent in the resin kettle equipped with N_2 gas line and condenser. After purging the reactor with N_2 gas, the AIBN initiator was added slowly into monomer solution and stirred at 65ºC for 6h. Alkali developable polymer matrix was obtained by precipitation by n-hexane, filtration and drying.



Scheme 4. Polymerization of alkali developable polymer matrix.

TABLE 2. Synthetic data of binder polymers

Sample	Composition					Conv	Mw	A/ V
	BMA	MMA	MAA	GMA	2-HEMA	(%)	($x10^3$)	
BP2-1	60	-	30	10	-	62.5	22	100
BP2-2	55	-	5	30	10	Gel	-	-
BP2-3	30	30	30	-	10	90.8	110	128
BP2-4	35	30	25	-	10	90.2	70	120
BP2-5	40	30	20	-	10	88.8	42	111
BP2-6	30	25	35	-	10	80.6	46	120
BP2-7	30	25	30	5	10	80.4	52	132

Of the binder polymers shown in Table 2, the binder polymer BP2-5 was found to give fine interdielectric layer pattern with optimum acid value of 111 and molecular weight of 4.2×10^4 g/mol.

2.4 Photolithographic Process

Photosensitive solution for patterning of interdielectric layer was spin-coated on ITO-coated glass followed by soft baking at 120ºC for 3 min. The dried film was exposed to UV light (100-300 mJ) 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.

3. Results and Discussions

3.1 Pattern Formation by Photolithographic Process

A negative-type photosensitive solution for patterning of interdielectric layer on TFT-LCD array was formulated with photo initiator (HSP188), photo-monomer (Imide UV monomer: TTG, ODG and PFA), photo-oligomer (EB-600), polymeric binder (alkali developable polymer matrix) as shown in Table 3. After optimization of formulation the negative-type photosensitive solution was found to give rectangular-type hole pattern (10μm x 10μm) with good resolution through the photolithographic process as shown in Fig.1 [1].

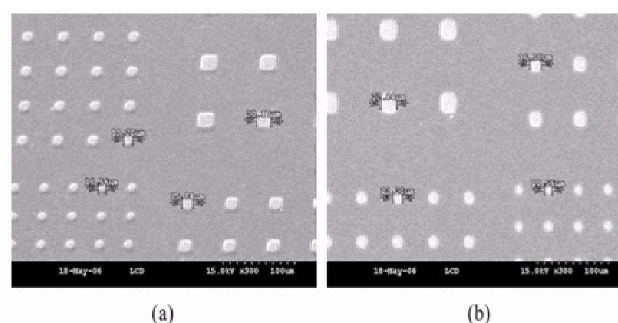


Fig.1. SEM photographs of patterned images; (a)using PS-TTG, (b)using PS-ODG formulation

3.2 Transmittance of Interdielectric Layer after Photolithographic Process

High transmittance is desirable for the interdielectric layer in TFT-LCD array. However, the application of polyimide type film for the interdielectric layer of TFT-LCD array was hampered by its yellowing properties. In this study, a new type of imide UV monomer containing imide core and double bonds for crosslinking were used to decrease the yellow color in the dielectric layer. As shown in Fig.2 the photosensitive solution especially PS-TTG gave high transmittance in the visible region. This might be due to the prevention of stacking imide moiety by the presence of bulky $-CF_3$ group in the imide core of the UV monomer.

TABLE 3. Formulation of photosensitive solution for interdielectric layer patterning.

Material/ Formulation	PS-TTG	PS-ODG	PS-PFA
	Ratio (wt%)	Ratio (wt%)	Ratio (wt%)
Photo initiator (HSP-188)	1.30	1.30	1.30
Photo monomer (Imide monomer)	6.50	7.50	7.00
Photo Oligomer (EB-600)	6.50	8.00	8.50
Binder Polymer	15.87	16.20	16.50
Solvent (DMF)	69.83	67.00	66.70
Total	100.00	100.00	100.00

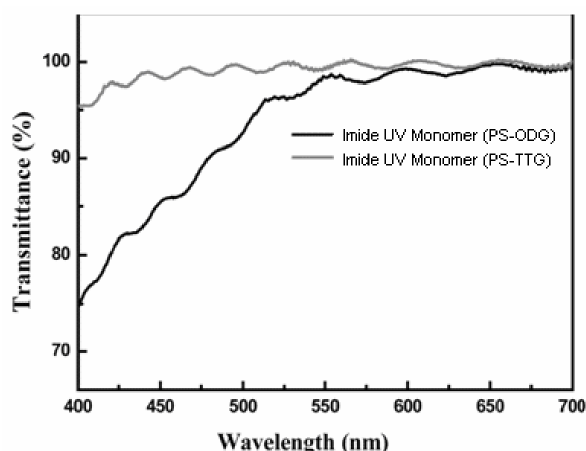


Fig.2. Transmittance spectra of interdielectric layer thin-film containing UV monomer with imide core.

4. Summary

Different types of UV monomers were successfully synthesized and characterized. Formulations consisting of UV monomers, photoinitiator, UV oligomer and alkali developable polymer matrix were optimized for photolithographic process. Pinhole pattern with good resolution (10 x 10 μm) was achieved using the optimized formulations. Moreover, formulation PS-TTG photosensitive solution with –CF3 groups in the imide core exhibited over 90% of transmittance in the visible region.

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5. References

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