Synthesis and characterization of negative-type photosensitive polyimides for TFT-LCD array

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Abstract

Two different negative-type photosensitive polyimides were synthesized and characterized for an application as an interdielectric layer in TFT-LCD array. In the case of photocurable polyimides, the photosensitive moiety, 2-HHSP, was synthesized through 3 step reaction, and then was incorporated into side chains of polyimide precursor by post reaction. Optimum compositions of negative-type photocurable polyimde were also formulated. For photopolymerizable polyimides, two novel UV monomers containing imide linkages were prepared. An aqueous alkaline developable polymer matrix was synthesized by free radical copolymerization. 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 transistor (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, characterization, and formulation of negative-type photocurable and photopolymerizable polyimides for an application as an interdielectric layer in TFT-LCD. Optimum photolithographic processes using these negative photoresist formulations were also determined.

2. Experimental

2-1. Materials

1,2,4,5-Benzenetetracarboxylic dianhydride, trimellitic anhydride, 4,4'-(hexafluoro-isopropylidene)diphthalic anhydride, 2-hydroxy ethyl acrylate, 3,3'-diamino-4,4'-dihydroxy biphenyl, 4,4'-Diaminodiphenyl ether, 2,2'-bis(3-amino-4-hydroxyphenyl) hexa fluoro propane were purchased from Aldrich Chemical Co. Trimellitic anhydride, 4,4’-diaminodiphenyl ether, 2,2’-bis(3-amino-4-hydroxyphenyl) hexa fluoro propane, acryloyl chloride, triethylamine, m-cresol, benzylmethacrylate, methacrylic acid were purchased from Aldrich Chemical Company. All other chemicals were also reagent grades and used as received.

2-2. Photolithographic process

Negative photoresist formulation for interdielectric layer patterning was spin-coated on ITO-coated glass, followed by soft baking at

120 ℃ 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).

3. Results and Discussion

3-1. Synthesis of negative-type photocurable polyimides

3-1-1. Synthesis of photosensitive moiety[1],[2]

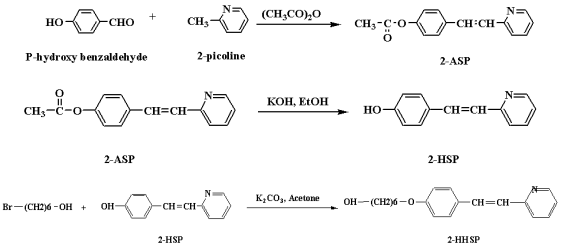
The reaction procedure is presented in Scheme 1. In the first step, acetoxystyryl-2-pyridine (2-ASP) was recrystallized from ethanol. In the second step, hydroxystyryl-2-pyridine (2-HSP) was recrystallized from ethanol. NMR (DMSO-d$_6$), ppm: 6.9-7.7 (-c=c-). 7.5-7.8 (Ar CH). 8.5 (Ar NH).

In the third step, photosensitive 2-HHSP was recrystallized from acetone/ethanol. NMR (DMSO-d$_6$), ppm: 7.1-7.3 (-c=c-). 7.0-7.6 (Ar CH). 8.5 (Ar NH). 3.3-4.2 (Aliphatic CH). 1.2-1.9 (Aliphatic CH). 4.3 (OH).

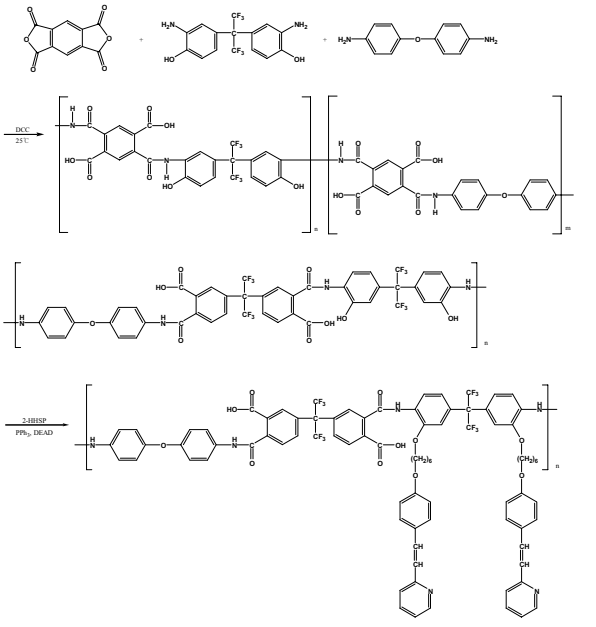
3-1-2. Synthesis of negative-type photocurable polyimide matrix[3],[4]

The reaction procedure is presented in Scheme 2. 1,3-Dicyclohexylcarbodiimide was slowly added into 1,2,4,5-benzenetetracarboxylic dianhydride dissolved in NMP, and stirred at room temperature for 2 hrs. After cooling down to 0 ℃, 2,2'-bis(3-amino-4-hydroxyphenyl) hexa fluoro propane and 4,4'-diaminodiphenyl ether were sequentially added, followed by the reaction at room temperature for 8 hrs. Polyimide precursor was obtained by filtration and dry.

Polyimide precursor, triphenyl phosphine and 2-HHSP were dissolved in THF. After cooling down to 0 ℃, diethyl azodicarboxylate was added while stirring. Then, Mitsunobu reaction was carried out at 25 ℃ for 72 hrs.



<Scheme 1>



<Scheme 2>

3-1-3. Pattern formation by photolithographic process

Results on solubility of synthesized photocurable polyimide precursors are summarized in Table 1.[5] Then, optimum composition for negative-type photocurable polyimide was formulated, as shown in Table 2. As can be seen in Figure 1, this composition was found to yield stripe-type and well-type polyimide patterns with good resolution.

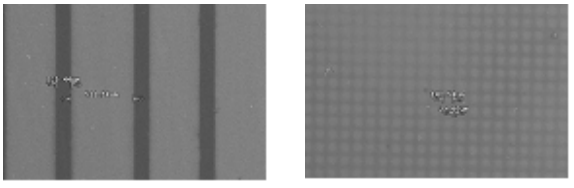
Table 1. Solubility of PAA with various solvents at room temperature.

	DMSO	DMF	γ-butyro -lactone	THF	NMP
PAA	O	◎	X	O	◎

◎:Good-Soluble, O:Soluble, X:Insoluble
DMSO: Dimethylsulfoxide, DMF: N,N-Dimethylformamide
THF: Tetrahydrofuran, NMP: N-methyl-2-pyrrolidone

Table 2. Formulation for interdielectric layers

	g	wt%
PAA	1.363	32.00%
NMP	2.897	68.00%
Total	4.26	100.00%



(A) (B)

Figure 1. SEM photographs of of patterned images; (a) stripe type and (b) well type.

3-2. Synthesis of negative-type photopolymerizable polyimides

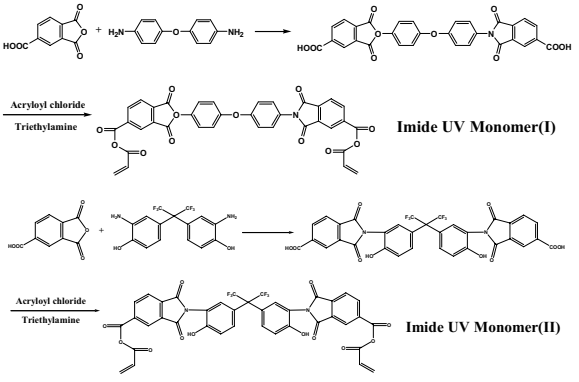
3-2-1. Synthesis of UV monomer with imide linkage

The reaction procedure is shown in Scheme 3. In the first step, trimellitic anhydride was added into m-cresol, and stirred at 150 ℃ for 30 min., and then 4,4'-diaminodiphenyl ether was slowly added and stirred at 150 ℃ for 6 hrs. Imide UV monomer precursor was obtained by washing with water, filtration and drying. In the second step, imide UV monomer precursor was reacted with acryloyl chloride dissolved in NMP with slow addition of triethylamine by stirring at room temperature for 2 hrs. After reaction, triethylamine salt was removed by filteration. The imide UV monomer(I) was obtained from the filterate by precipitation with 1% HCl aqueous solution, followed by filteration and drying. *FT-IR(v in Cm^{-1}) : 912(aromatic imides), 713 (=CH γ oop).*

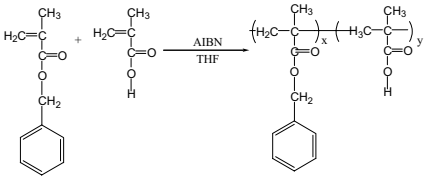
Imide UV monomer(II) was prepared by similar process with 2,2-Bis(3-amino-4-hydroxyphenyl) hexafluoropropane and trimellitic anhydride. *FT-IR(v in Cm^{-1}) : 915(aromatic imides), 708 (=CH).*

3-2-2. Synthesis of alkali developable polymer matrix

The reaction procedure is presented in Scheme 4. Benzylmethacrylate (58.886g, 0.334mol) and methacrylic acid (12,317g, 0.143mol) monomer were dissolved in THF (280ml), and stirred for 6 hrs at 65℃ with AIBN (1.570g, 0.01mol) as initiator. Alkali developable polymer matrix was obtained by precipitation in n-hexane nonsolvent, followed by filtration and drying. *FT-IR (v in Cm^{-1}) : 1798 (C=O st, carbonic acid), 1178 (C-O st carbonic acid).*



<Scheme 3>



<Scheme 4>

3-3 Interdielectric layer pattern formation by photolithographic process

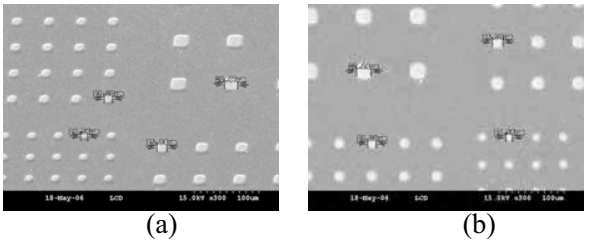
A negative type photoresist formulation for the patterning of interdielectric layer in TFT array is shown in Table 3. In this formulation the crosslinking reaction in the UV irradiated region

was obtained by the photopolymerization of synthesized UV imide monomer and commercial UV oligomer with photoinitiator(HSP 188), while alkali soluble binder polymer was used for the development of the UV unexposed region.

Table 3. Formulation for interdielectric layer

	Test-1		Test-2	
	g	wt%	g	wt%
Photo Initiator (HSP188)	0.065	1.30%	0.065	1.30%
Photo Monomer (Imide monomer)	0.325	6.50%	0.325	6.50%
Photo Oligomer (EB-600)	0.325	6.50%	0.325	6.50%
Binder Polymer (Poly(BzMA-co-MAA)	0.795	15.87%	0.795	15.87%
Solvent (DMF)	3.49	69.83%	3.49	69.83%
Total	5	100.00%	5	100.00%

It was found that Test-2 photoresist gave both high transmittance in the visible range and thermal resistance compared to Test-1 formulation due to the presence of CF_3 groups in the imide UV monomer(II). The photolithographic patterning of interdielectric layer for TFT array was obtained in good resolution with both formulations as shown in Fig. 2.



(a) (b)

Figure 2. SEM photographs of patterns obtained with (a) Test-1 and (b) Test-2 photoresist formulation

4. Conclusion

Negative-type photocurable polyimides for an interdielectric layer in TFT-LCD array were successfully synthesized and characterized. They also provided good stripe-type and well-type patterns of polyimide layers by conventional photolithographic process. In the case of photopolymerizable polyimides, UV curable monomers with thermally stable imide linkage were synthesized. A negative photoresist formulation was developed utilizing the imide UV monomer, conventional UV oligomer, photoinitiator and aqueous alkali developable binder polymer. This negative photoresist was also found to give good patterning of interdielectric layer for TFT array by photolithographic process.

5. Acknowledgements

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6. References

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