Positive Type Photoresist for Patterning of Interdielectric Layer of TFT Array

 Hyo-Jung Lee¹, Hyo-Jin Kim¹, Soon Hak Kim¹, Lee Soon Park^{1,2}, , Yun Su Lee², Gab Deuk Song²
 ¹Dept. of Polymer Science, ² Mobile Display Research Center, Kyung pook National University, Daegu, 702-701, Korea
 Phone: +82-53-950-5627, E-mail: lspark@knu.ac.kr

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Abstract

Synthesis of two photoactive compounds containing core imide moiety was carried out for an application to interdielectric layer in TFT-LCD array. An aqueous alkaline developable polymer matrix was synthesized by free radical copolymerization. A positive photoresist formulation was developed utilizing synthesized UV monomers, photoactive compound, binder polymer, sulfactant 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 new positive interdielectric material with high thermal stability.

1. Introduction

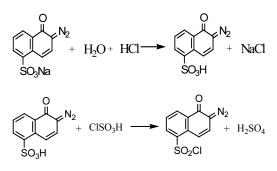
Thin film transistor (TFT) is a switching device consisting of source and drain electrodes, gate electrode, interdielectric layer, and active semiconductor layer. The requirements for the interdielectric layer of TFT include relatively low

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 photo patterning 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 the synthesis of new photoactive compound and UV monomers and formulation of positive-type photoresist for an application to interdielectric layer in TFT array. Optimum photolithographic process using this positive photoresist formulation was also examined. [1], [2]

2. Experimental

2-1. Synthesis of 1, 2-Naphthoquinone-2-diazo-5-sulfonyl chloride.

The reaction procedure is shown in Scheme 1. In the first step, 1N-HCl solution was slowly added into NQD-SO₃Na aqueous solution, stirred for 30 min, and the reaction product, NQD-SO₃H was obtained by washing with water, filtration and drying. In the second step, chlorosulfonic acid was added slowly into NQD-SO₃H solution and the mixture was stirred at 50 °C for 5 hr. After reaction, NQD-SO₂Cl was obtained by filteration, washing with water and drying.

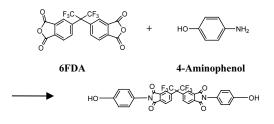


<Scheme 1> Synthesis of NQD-SO₂Cl

2-2. Synthesis of Ballast

The reaction procedure is shown in Scheme 2. First 4-aminophenol was slowly added into the 6FDA in NMP solution in the ice-bath. After reaction for 12hr at room temperature, xylene was added into the reaction mixture and stirred at 160 $^{\circ}$ C for 5hr with removal of water. The resulting solution was poured into 1N aqueous HCl solution and the solid product was filtered and washed with water.

The product washed with THF and dried in vacuum at 100° C for 20hr.



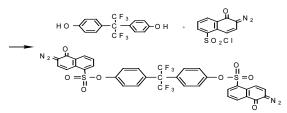
Ballast with imide units

<Scheme 2> Synthesis of ballast with imide units

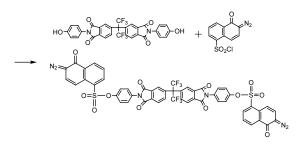
2-3. Synthesis of Photoactive Compounds

The reaction procedure is shown in Scheme 3. Hexafluorobisphenol A and NQD-SO₂Cl were dissolved in 1,4-dioxane and triethylamine dioxane solution was slowly added at 35 $^{\circ}$ C and stirred for 2hr. After reaction thriethylamine, hydrochloride salt was removed by filteration. Photoactive compound (I) was obtained by Filtration washing and with 1% HCl aqueous solution, followed by filtration and drying. [3]

Photoactive compound (II) was prepared by similar process with the synthesized ballast as shown in Scheme 3.



Photoactive Compound (I)

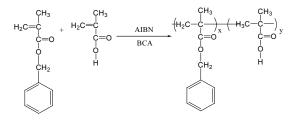


Photoactive Compound (II)

<Scheme 3> Synthesis of photoactive compounds.

2-4. Synthesis of Polymer Matrix

The polymerization reaction is shown in Scheme 4. Benzylmethacrylate and methacrylic acid monomer were dissolved in BCA solvent, and stirred for 6 hr at 65 °C with AIBN as initiator. Alkali developable polymer matrix was obtained by precipitation in n-hexane as nonsolvent, followed by filtration and drying. FT-IR(v in cm⁻¹) : 1798(C=O st, carbonic acid), 1178(C-O st carbonic acid)

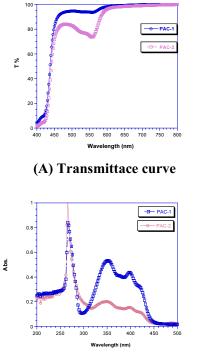




3. Results and Discussion

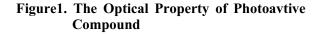
3-1. Optical Properties

The newly synthesized photoactive compounds (I,II) were examined for the optical property with the UV-visible spectrometer. As Shown in Fig.1 both photoactive compound (I and II) exhibited high transmittance in the visible light range. The photoactive compound (II) had higher absorbance in the UV range due to the presence imide units in the molecular structure.



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(B) Absorbance curve



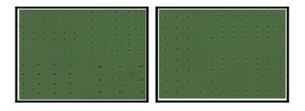
3-2. Formulation of Photoresist and Photolithographic Process

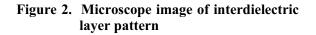
A typical formulation for the positive type photoresist for the interdielectric layer patterning is shown in Table 1. In this Table photosensitive interdielectric materials (PIM-1 and PIM-2) were obtained by mixing photoactive compound (I) and (II) with binder polymer solution, surfactant and solvent, respectively.

Table 1. Formulation of photosensitive interdielectric materials

Interdielectric	PIM-(I)		PIM- (II)	
material	g	wt%	g	wt%
photoactive compound (I),(II)	0.3	3.00%	0.3	3.00%
Binder Polymer (Poly(BzMA-co-MAA)	6	18.00%	6	18.00%
sulfactant	0.1	1.00%	0.1	1.00%
Solvent (DMF)	3.6	78.00%	3.6	78.00%
Total	10	100.00%	10	100.00%

The photolithographic patterning of interdielectric layer for TFT - array was obtained in good resolution up to $10*10 \ \mu$ m pattern size as shown in Fig.2.





4. Summary

A positive type photoresist for interdielectric layer patterning of TFT array was developed utilizing the newly synthesized photoactiveactive compound and matrix polymer. The positive photoresist was found to give good patterning of interdielectric layer up to 10 µm size by photolithographic process. The new positive interdielectric material had high thermal resistance and good optical property after patterning process.

5. References

- [1] Steve Lien-Chung Hsu, Ming Hsin Fan, Polymer 45, 1101-1109 (2004)
- [2] Larry F. Thomson, C. Grant Willson, and Seiichi Tagawa, "Polymers for Microelectronics, Resist and Dielectrics", ACS, ch. 26, Washington, DC, (1994).
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