Dye-Containing Methacrylic Polymers in the Composition of Photo Resists for Complementary Metal Oxide Semiconductor Image Sensors

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Abstract

The trend in the development and manufacturing of Complementary Metal Oxide Semiconductor (CMOS) image sensors is to miniaturize pixels on the chips and hence to improve their imaging characteristics by providing a higher image resolution. As CMOS technology scales down into submicron regions, the conventional color filters are no longer suitable for generating the desired optical density. The major drawback of the conventional color filters produced from pigment-based positive tone photosensitive compositions, is the heterogeneous dispersion of pigments in photoresist composition resulting in color irregularities due to coarse particles of the pigments. One of the most perspective ways to solve this problem is a replacing the pigment with a dye as a coloring agent and thus, increasing solubility of the latter to obtain a homogeneous colored photoresist composition.

In this paper, several novel red dye-containing materials are synthesized and tested to provide a red-colored photosensitive composition. This red-colored photosensitive composition is very promising for application as color filters for CMOS image sensors with high resolution and high level of integration architecture.

Introduction

Image sensors technologies such as Charge Coupled Device (CCD) and Complementary Metal Oxide Semiconductor (CMOS) have received much attention in recent years and are widely used in fast growing digital imaging industries. There are many different types of imaging system suitable for different applications, such as digital still cameras, digital camera for cell phones, camcorders, webcams, security cameras, computer, etc. With the evolution and progress of digital imaging industries, design and development of new materials with high performance and improved functional capability, CMOS image sensor technology is becoming more and more popular due to many advantages over CCD systems. Main of them are low power consumption, low voltage operation, low cost, on-chip functionality and compatibility with standard CMOS technology, random access of image data, high-speed imaging, miniaturization, and there are many more others. Despite these advantages, there are still lots of work to do in order to improve resolution, sensitivity and image quality of CMOS sensors. It would be especially difficult for new scale-down technologies and architectures such as cellular phones, computer video, space and medical photography, 3D applications, etc.

Color filters used in CMOS image sensors should follow this trend and therefore their pixel size should be reduced. Thus, with the reduction of pixel size, the CCD having plurality of red, green and blue pixels can be miniaturized and the number of pixels mounted on CCD can be increased to provide image information with high resolution.

Photolithography technique for generating color filters using pigment-based color resists could not provide fine micro pixel size less than 2μm. This limitation is mainly due to particle size of pigments, resulting in color irregularities caused by coarse particles. This problem, however, could be solved if pigments are replaced by a soluble coloring material in the color resist composition.

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Some research groups [1-2] focused their efforts on the selection of organic dyes and investigated their properties and practical uses in submicron color filters development. Although, dyes are more soluble than pigments providing a homogenous solution in photoresist composition, they generally do not have good thermal, light and chemical stability when compared to pigments. However, one could imagine enhancing thermal, light and chemical stabilities of dyes if they are incorporated in a polymeric structure as pendant groups. Recently, incorporation of a dye moiety into a polymer structure has been a subject of interest to many research groups and for various purposes such as synthesis of photoactive polymers [3], non covalent interactions between dye molecules and polymers in optical storage field [4], as well as improvement of color fastness of polymers [5], etc.

In this paper, we discuss a design strategy and synthetic method development of a new class of red anthraquinone-containing copolymers. In addition, we examine different properties of these novel copolymers used in the composition of color resists and illustrate photo patterning results.

Experimental

Synthesis of dyed monomers

1) A solution of Chloroanthraquinone (1.0 equiv.), aminoalkyl alcohol (3.0 equiv.) in N-methylpyrolidinone (NMP) was heated at 80 ^{o}C under nitrogen atmosphere until completion of the reaction. The reaction mixture was then cooled to room temperature and precipitated in water. The resulting solid was filtered, washed with water and re-crystallized in acetonitrile to give the corresponding pure hydroxyl alkylamino-anthraquinone.

2) To a solution of hydroxyl-alkylamino-anthraquinone (1.0 equiv.), methacrylic anhydride (1.2 equiv.), N, N-dimethyl amino pyridine (DMAP) (0.2 equiv.) in tetrahydrofuran (THF), triethylamine (TEA) (1.3 equiv.) was added over a period of 30-40 minutes. The mixture was stirred at room temperature until the reaction was completed. Acetic acid was then added and the solution was precipitated in water. The resulting solid was filtered, washed with water and re-crystallized in acetonitrile to give the desired dyed monomer.

Synthesis of dyed copolymers

To a solution of the dyed monomer (5.0 g) in THF, was dropwisely added a solution of methacrylic acid (1.0 g), benzyl methacrylate (4.0 g), 2,2'-Azobis(2-methylpropionitrile) (AIBN) (0.7 g) in THF at 60 ^{o}C under nitrogen atmosphere. The mixture was stirred for 6 hours at 60 ^{o}C and then cooled to room temperature. The resulting mixture was slowly poured into n-hexane under vigorous stirring, and the thus formed precipitate was filtered, rinsed and dried under vacuum.

Formulation of color resists

Methacrylic ester copolymer (0.33 g), base copolymer (2.68 g), Dipentaerythrithol hexaacrylate, a photoinitiator of triazine type (0.14 g) and 8.53 g of a mixture of propylene glycol monomethyl ether acetate, ethyl 3-ethoxy propionate and cyclohexanone were stirred at room temperature to obtain a clear red solution.

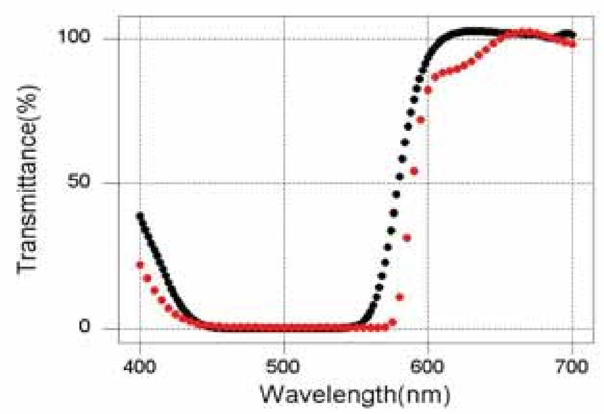


Fig. 1. The transmittance spectra of Solvent Red 111(black) and Pigment Red 254(red)

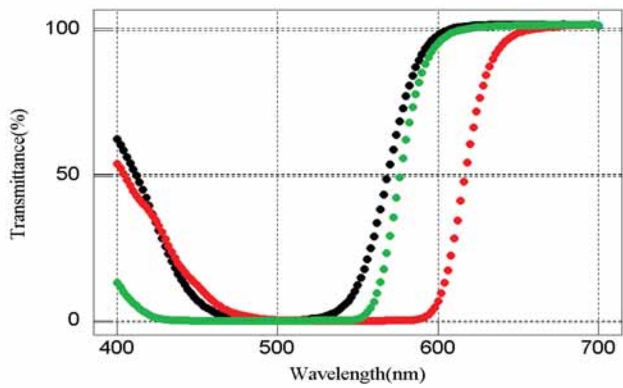


Fig. 2. Transmittance spectra of 1C(black), 2C(green), and 7C(red) methacrylic dye monomers.

Photo-patterning

The red-dyed color resist was spin-coated on a 200 mm silicon wafer to give a film of 6000 Å in thickness. The thus obtained coated wafer was soft baked at 100 °C for 180 s, exposed at I-line (365 nm; mask size : 1.4) for 100 - 1,000 ms, then developed by 0.2 % tetramethylammonium hydroxide aqueous solution for 120s, and finally baked at 200 °C for 300 s. The patterns were observed by scanning electronic microscopy (SEM).

Results and Discussion

In order to select red dyes of similar coloring properties as conventional red pigments such as Pigment Red 254 used in color resist composition, a number of commercially available dyes such as solvent red 111, 119, 122, 124, 160 and solvent red 179 were chosen for initial screening, and their transmittance spectra were measured. Among these dyes, solvent red 111 (Anthraquinone class) transmittance spectra matched the target spectrum to a large extent, as shown in Fig. 1. Therefore it was selected as a model dye for the synthesis of a red dye-containing metharcylic monomer.

Attempts to synthesize an anthraquinone-containing methacrylic monomer by reacting solvent red 111 or 1-amino anthraquinone with methacrylic anhydride or methacryloyl chloride failed and only the starting materials were recovered. The failure of these reactions could be attributed to hydrogen bonding between the proton attached to amine group and the adjacent oxygen atom of the carbonyl group, which considerably reduces the reactivity of the amine group of the anthraquinone moiety towards nucleophilic substitutions.

The second method proposed for preparing anthraquinone-containing methacrylic monomer is the reaction between chloro anthraquinone (A) with an aminoalkyl alocohol (B) to yield the corresponding hydroxyalkylamino anthraquinone which, in turn, is reacted with methacrylic anhydride in the presence of a base to provide the expected monomer (C) (Table 1). This synthetic method was found to be very efficient, and the red anthraquinone-containig methacrylic monomers were obtained with high yield.

The transmittance spectra of the thus prepared monomers listed in Table 1 were measured in UV-Vis region between 400-700 nm and compared to that of solvent red 111, as shown in Fig. 2. It was noted that, with the exception of 3C, transmittance spectra of the methacrylic dye monomers were similar to that of solvent red 111.

Table 1.
Synthetic schemes of methacrylic dye monomers

A + B → C
1) 80°C, 1hr, NMP
2) Methacrylic anhydride TEA, DMAP, rt, 1hr, THF

	A	B	C
1	O, Cl (1-chloroanthraquinone)	H_2N … OH	O, HN, O, O, O
2		H_2N … OH	O, HN, O, O, O
3		N(H) … OH	O, N, O, O, O

	A	B	C
4		H_2N – OH	O, HN, O, O, O
5	O, Cl, Cl, O	H_2N – OH	O, HN, O, O, O, O, NH, O
6		H_2N – OH	O, O, O, HN, NH, O, O, O
7	Cl, O, Cl, O	H_2N – OH	O, NH, O, HN, O, O, O, O

The dyed copolymer was prepared by free radical copolymerization of three different methacrylic monomers, namely the red anthraquinone-based methacrylate, methacrylic acid and benzyl methacrylate. Methacrylic acid was used for its solubility in a developer - an alkaline aqueous solution such as tetramethylammonium hydroxide solution. In fact, after photo patterning (365 nm), the color resist at unexposed regions should be base soluble, and be fully removed by the developer to produce the desired patterns. Benzyl methacrylate was used to increase the solubility of the resulting copolymers in the formulation.

The polymerization was carried out in THF at 60 °C under nitrogen atmosphere in presence of 7.0 mol % of AIBN. After 6 hours, the reaction was quenched by cooling to room temperature. The resulting polymer was purified by precipitation is n-hexane. The weight averaged molecular weights (Mw) and polydispersity (PDI) of the copolymers were measured by gel permeation chromatography, and are given in Table 2.

The photo resists derived from these dyed copolymers were spin coated on silicon wafers and baked to produce a homogeneous film. After photopatterning at 365 nm using 1.4 μm square shape mask followed by development in the developer solution, the patterns were examined by scanning electronic microscopy (SEM). The top view SEM images of these dyed color resists are given in Fig. 3. A high quality, residual-free square shape patterns are seen, while the patterns formed from pigment containing color resists showed many defects such as bumps, bridging, irregular size, etc. (not shown).

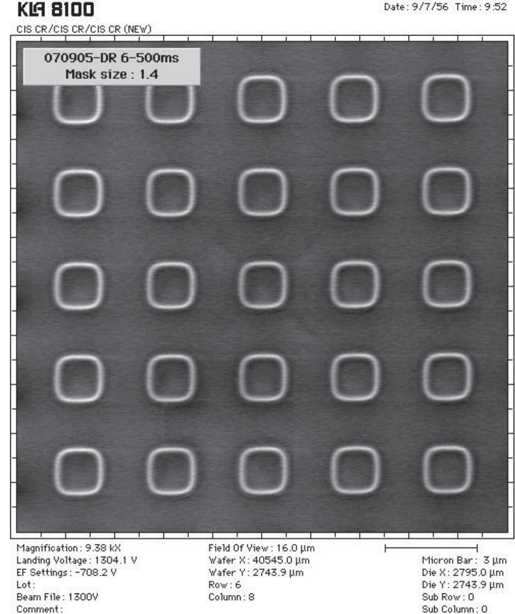
Table 2.
Molecular weights of dyed polymers characterized by Gel Permeation

Chromatography

Methacrylic Dye Monomer + BzMA + MAA $\xrightarrow[\text{solvent}]{\text{AIBN}}$ POLYMER

Methacrylic Dye Monomers	Mw	PDI(a)
	19,986	1.71
	5,632	1.65
	20,592	1.57
	15,957	1.62

(a) PDI : Polydispersity



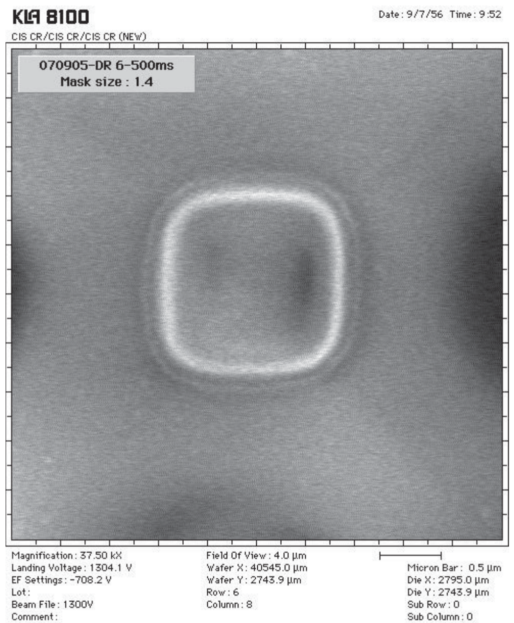


Fig. 3. The SEM images of 1.4μm patterns formed by lithography using dyed color resist.

Conclusion

In this paper, design and preparation of a number of novel red anthraquinone-based methacrylic monomers having similar dye properties as that of current red pigments used in CMOS technology have been presented. Copolymers derived from these monomers were used in the composition of red dye color resists. It is shown, that I-line lithography process of these color resists allows to produce fine, residual-free, 1.4 μm pixel size squared patterns on silicon wafer.

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