Diphenyliodonium Salts with Diazoxide Group for a Photo-acid Generator in Chemically Amplified Resist

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1. Introduction

Chemically amplified resists based on acid catalyzed reaction have been widely utilized in the development of semiconducting technology and resists. Photo-acid generator (PAG) that generated acids upon irradiation with light played an important role on the progress of chemically amplified resist. Various onium salts were applied as PAGs in photolithography [1,2,3].

Onium salts as a photo-acid generator have several advantages such as various combination of anion parts and easy structure modification to alter their spectral absorption. Then these PAGs which have photosensitivity at 193 nm or 248 nm have been studied, however there were a few reports [4] about the onium salt's PAGs for 365 nm light.

In this study, we investigated a new type PAG (AZO-DPI, 1) which has a fine photosensitivity at 365 nm. The AZO-DPI has a cation of iodonium compound and an anion of diazoxide compound (AZO-SO₃Na, 2), that acts both spectral sensitizer for iodonium ion and precursor of acid, and can be applied to lithography.

2. Results and Discussion

Figure 1 shows the absorption spectra of AZO-SO₃Na and diphenyliodonium chloride

(DPI-Cl) and the fluorescence spectrum of AZO-SO₃Na in oxygen-free MeOH. AZO-DPI was synthesized by reaction of AZO-SO₃Na and diphenyliodonium chloride in water [5].

Fig 1. Absorption (—) and fluorescence (---) spectra of AZO-SO₃Na in MeOH. Absorption spectrum of DPI-Cl (●) in MeOH. The concentration of AZO-SO₃Na and DPI-Cl were 4.44×10^{-5} and 2.28×10^{-5} mol dm⁻³, respectively; excitation wavelength 365 nm in the fluorescence spectrum.

AZO-SO₃Na has the strong absorption at 235 nm, 243 nm and a broad absorption with vibrational structure in the wavelength region 260-450 nm and a broad fluorescence spectrum with vibrational structure in the wavelength region from 380 to 560 nm. The absorption of AZO-SO₃Na extends to longer wavelength than that of DPI-Cl. From these spectra, the lowest excited singlet energy (E_{00}) of AZO-SO₃Na was estimated to be 70.4 kcal/mol.

Figure 2 shows the absorption spectrum of AZO-DPI in oxgen-free MeOH.

Fig 2. Absorption (-) and fluorecence (---) spectra of AZO-DPI in MeOH. The concentration was $3.77 \times 10^{-5} \text{ moldm}^{-3}$ for AZO-DPI; excitation wavelength 365 nm in the fluorescence spectrum. Absorption coefficient at 365 nm: $4.03 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ for AZO-DPI.

The electrochemical behavior has been studied in DMF solution with tetrabutylammonium perchlorate as the supporting electrolyte [6]. The oxidation potentials ($E_{1/2 \text{ ox}}$) of AZO-SO₃Na was + 1.05 V vs SCE and the reduction potentials ($E_{1/2 \text{ red}}$) of DPI-CI was - 0.81 V vs SCE. Based on these values of redox potentials, the free-energy changes (ΔG) accompanying the electron transfer from the lowest excited single state of diazoxide moiety to DPI's can calculated according to the Rehm-Weller equation, where

$$\Delta G = 23.06 \{ E(D/D) - E(A^+/A) - C \} - E_{00}$$

 $E(D/D)$ is the oxidation potential of the doner. $E(A^+/A)$ is the reduction potential of the accepter. E_{00} is the electronic energy corresponding to the excited singlet state of the doner and C is the Coulombic interaction energy of 1-2 kcal/mol in the polar solvent.

In the AZO-DPI case, the value of ΔG is calculated to - 28 kcal/mol without considering the Couombic interaction. The results indicated that the intramolecular electron transfer from anion to cation depended on diffusion controlling.

AZO-SO₃Na was dissociated by irradiation at 365 nm. Then quantum yield of photodissociation from AZO-SO₃Na was determined from the absorption changes at 365 nm [7]. The quantum yield of photodissociation from AZO-SO₃Na was 0.43.

Fig 3. Spectral change upon irradiation of MeOH solution containing AZO-SO₃Na ($1.29 \times 10^{-4} \text{ moldm}^{-3}$)

The diazoxide structure of AZO-DPI was also dissociated by irradiation at 365 nm. Then quantum yield of photodissociation from the diazoxide structure for AZO-DPI was determined from the absorption changes at 365 nm [8]. The quantum yield of photodissociation from the diazoxide structure for AZO-DPI was 0.186.

Fig 4. Spectral change upon irradiation of acetonitrile solution containing AZO-DPI ($3.74 \times 10^{-5} \text{ moldm}^{-3}$)

The acid generation yield was measured using sodium salt of tetrabromophenol blue (TBPB) as an acid indicator [9]. Absorption band of TBPB at around 618 nm was changed by the addition of an acid quantitatively. Absorption changes of TBPB using *p*-toluenesulfonic acid as a standard material were calibrated. Quantum yield was determined from the absorption changes at 618 nm due to acid generation.

The quantum yield of acid generation from AZO-DPI was 0.211.

These results were associated that the acid generation mechanism for AZO-DPI has a few relation with the photodissociation of the diazoxide structure for AZO-DPI.

We carried the photolithographic evaluation [10] of the PAG. Figure 5 shows the relationship between the exposure dose and the normalized film thickness after development. The sensitivity at 365 nm of the new PAG was 120 mJ/cm².

Fig 5. Characteristic curves of the photopolymer involved AZO-DPI 3 wt%

This is a positive working resist which shows solubility change due to deprotection by irradiation and subsequent bake. SEM micrograph of pattern [11] from polymer with 3 wt% AZO-DPI is shown in Figure 6.

Fig 6. SEM photograph of pattern from poly(ethoxyethyl-PHS) with AZO-DPI.

We designed and presented the potential of the new PAG with diazoxide compound for 365 nm chemically amplified resist. The absorption coefficients at 365 nm for the new PAG, AZO-DPI were 10³ order, originating in diazoxide structure. The quantum yield of acid generation by irradiation of the 365 nm was 0.221. The photo-acid generating efficiency in polymer bearing ethoxyethyl protecting group was 120 mJ/cm². These results show that the AZO-DPI are promising PAG for 365 nm chemically amplified resists.

References and Notes

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5. AZO-DPI was prepared as follows. An amount of 0.5 g (1.84 mmol) of AZO-SO₃Na and 0.7 g (2.2 mmol) of DPI-Cl were dissolved in water each other. AZO-SO₃Na solution was dropped into DPI-Cl solution. Stirring at room temperature was continued for 2 h, and filtrated.; yield 0.8 g (82.0%) mp 144.2 °C (Decomposition temp.) ¹H-NMR (400MHz, DMSO) 6.99(1H,s), 7.27 (1H,m), 7.52(6H,m), 7.65 (2H,m), 8.23(4H,m) and 8.60(1H,d); IR (KBr pellet) 3225 cm⁻¹, 2050 cm⁻¹, 1610 cm⁻¹, 1560 cm⁻¹, 1475 cm⁻¹, 1445 cm⁻¹, 1220 cm⁻¹, 1054 cm⁻¹, 980 cm⁻¹, 745 cm⁻¹ and 650 cm⁻¹.
6. Redox Potentials were measured by cyclic voltammetry with Hokuto - Denko Function Generator HB-104 and apotensiostat/ galvanostat HA-301. Electrochemical measurements were carried out using a three-electrode cyclic voltammetric cell. The working electrode was a platinum wire and the reference electrode was calomel electrode. The electrolyte was 0.1 M tetrabutylammonium perchlorate in DMF. The voltammograms were scanned at 50 mVs⁻¹. All potentials are calculated vs SCE as E_{1/2} values, where E_{1/2} = 0.5(E_{pa}+E_{pc}) ; E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.
7. The 1.29x10⁻⁴ moldm⁻³ MeOH solution of AZO-SO₃Na in quartz cell was irradiated by the 365 nm light with a filtered super high-pressure mercury lamp. After irradiation, the absorption at 365 nm of the MeOH solution was measured. Irradiation time were 0 s, 5 s, 12 s, 20 s, 30 s, 45 s

and 60 s.

8. The 3.74×10^{-5} moldm⁻³ acetonitrile solution of AZO-DPI in quartz cell was irradiated by the 365 nm light with a filtered super high-pressure mercury lamp. After irradiation, the absorption at 365 nm of the MeOH solution was measured. Irradiation time were 0 s, 5 s, 12 s, 20 s, 30 s, 45 s and 60 s.

9. The 3.74×10^{-5} moldm⁻³ acetonitrile solution of AZO-DPI in quartz cell was irradiated by the 365 nm wavelength light with a filtered super high-pressure mercury lamp. After irradiation, 3 ml of the solution was mixed with 1 ml of 5.59×10^{-5} moldm⁻³ acetonitrile solution of TBPB and the absorption at 618 nm of the mixture was measured.

10. 1.0 μ m thick film consisted of

poly(ethoxyethyl-styrene) and 3 wt% PAG against polymer was prepared on silicon wafer and pre-baked at 95°C for 2 min. The exposure was carried out using an super high-pressure mercury lamp. Exposed resists were post-exposure baked at 95°C for 5 min on a hot-plate and developed in a 2.38 wt% TMAH solution for 14 s.

11. Photopolymer solution containing 3 wt% PAG against the polymer was spin-coated on silicon wafer to give a 1 μ m thickness film. The films were pre-baked at 95°C for 2 min and exposed 365 nm wavelength light with a filtered super high-pressure mercury lamp. PEB was carried out at 95°C for 5 min. They were developed in a 2.38 wt% TMAH solution.