Photosensitization of Base-Developable Poly(phenylhydrosilane) with 3,3′,4,4′-Tetra(*tert*-butylperoxycarbonyl)benzophenone. Mechanism of the Drastic Photosensitization in Terms of Photoinduced Electron Transfer

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ABSTRACT: A likely mechanism of especially large photosensitization for a base-developable poly(phenylhydrosilane) resist (**1**) in the presence of 3,3′,4,4′-tetra(*tert*-butylperoxycarbonyl)benzophenone (EA1) is discussed in terms of photolysis rates and dissolution rates. The increase in the photolysis rate occurs through photoinduced electron transfers from polysilanes to electron acceptors. The fluorescence quenching rate of **1** in the presence of EA1 is almost the same as that in the presence of benzophenone (EA2). However, EA1 does increase both photolysis rates and resist sensitivities, but EA2 does not. The difference between EA1 and EA2 is discussed in terms of back-electron transfer in order to explain the importance of the presence of peroxide moieties. In the case of EA2, photoinduced electron transfers as well as back-electron transfers occur. In case of EA1, the cleavage of peroxide bonds on the benzophenone moiety would effectively inhibit the back-electron transfer to the **1** radical cation. The same phenomena are observed for C-60. EA1 photodecomposes to form compounds bearing carboxylic acids which also facilitate the dissolution of photolysis products of **1** into basic aqueous solutions.

Introduction

Polysilane resists have been investigated extensively as a bilayer polysilane resist necessary in LSI devices.[1,2] Resist patterns are fabricated by UV exposure, followed by development. A KrF excimer laser (248 nm), a ArF excimer laser (193 nm), and X-rays have been reported to be useful light sources for polysilane lithography.[3−24] Miller et al. have reported that certain halogenated additives, such as a chlorinated triazine (EA5), enhance the photosensitivity of certain polysilanes, so that the needed dose approximates that in LSI production lines.[2,5−8,15]

Conventional alkyl- and aryl-substituted polysilane resists had to be developed with organic solvents such as alcohol/methyl ethyl ketone mixtures,[2,5−8,15] which is not compatible with currently conducted production lines, where dilute basic aqueous solutions have been employed. While a dry etching development by employing HBr in a vacuum chamber has been recently reported,[10,12,13,16,18] a facile and environmentally friendly development process with an aqueous base solution is still needed.

Polysilanes bearing phenols and carboxylic acids have been reported to be developable with tetramethylammonium hydroxide (TMAH) aqueous solutions.[25−27] In these resists, however, acidic moieties had to be placed in the side chains of the polysilanes to afford base solubility. The introduction of these functional groups was not easy.

We have reported for the first time that poly(phenylhydrosilane) (**1**) not bearing acidic moieties provides polysilane resists developable with basic aqueous solutions.[28] When UV light is exposed to **1**, **1** photodecomposes to form oligomers having silanols bearing phenyl groups which are soluble in basic aqueous solutions.[29−33] In the course of this study, we found that 3,3′,4,4′-tetra(*tert*-butylperoxycarbonyl)benzophenone (EA1) increased drastically the sensitivity of resist **1** from 1100 to 100 mJ/cm^2. The effect was more than those of other electron acceptors reported in previous papers.[28,34,35] The results are summarized in Table 1, briefly.

Table 1. Brief Results on Photosensitizers[28]

	resist sensitivity[a] (mJ/cm^2)	photolysis rate[b]
	1100	1
EA3	1100	1.2
EA5	800	1.5
EA1	100	1.8

[a] Developments were carried out with 2.38% tetramethylammonium hydroxide aqueous solution.[28] [b] Relative photolysis rates when **1** was exposed at 200 mJ/cm^2 (254 nm). Details are described in ref 28.

In this article, why the increase in the sensitivity of the polysilane **1** resist is so remarkable in the presence of EA1 is discussed in terms of photoinduced electron transfers and photolysis products of EA1. Especially, the discussion is focused on back-electron transfers. To explain the importance of the presence of peroxides bonded on benzophenone moieties, fluorescence quenching rates, photolysis rates, and resist sensitivities of **1** in the presence of EA1 were compared with those in the presence of EA2.

Experimental Section

Materials. Poly(phenylhydrosilane) (**1**) was synthesized according to the methods reported by Li et al.[36] **1** has bimodal molecular weight distributions. These molecular weights were 2500 and 1000, respectively. Poly(methylphenylsilane) (**2**) was prepared by the Wurtz coupling reaction.[37] The M_w of **2** was 12 000. Tetramethylammonium hydroxide (TMAH) aqueous solution (2.38%) was employed as a developer. 3,3′,4,4′-Tetra(*tert*-butylperoxycarbonyl)benzophenone (EA1) was purchased from Nippon Oil and Fats Co. and used without further purification. Other electron acceptors and an acid indicator, tetrabromophenolblue sodium salts (AI), are commercially available and used without further purification. The abbreviations of these materials are summarized in Figure 1.

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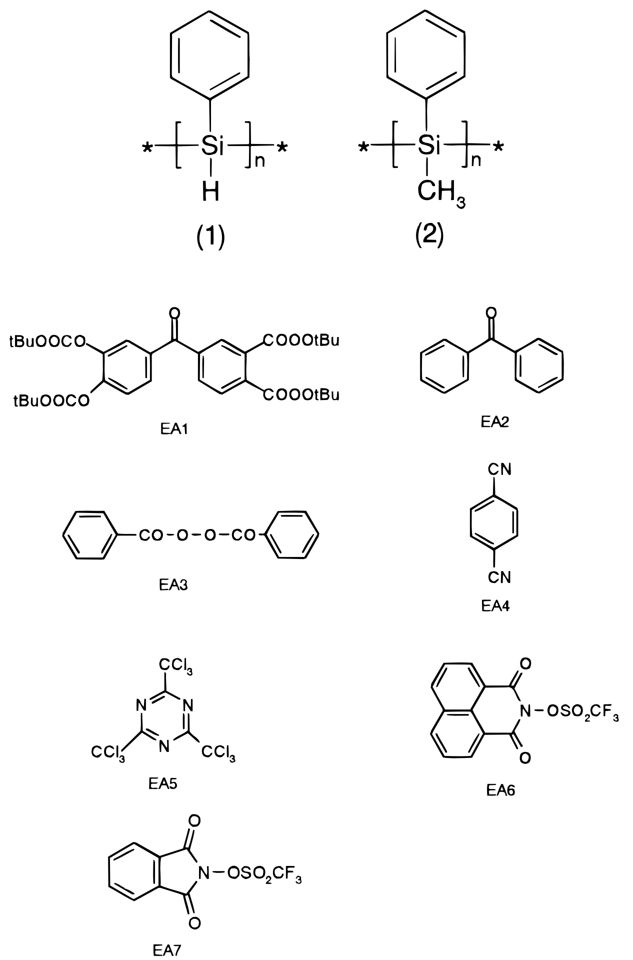


Figure 1. Abbreviations for polysilanes and electron acceptors.

Photolysis. Polysilane in toluene was spin-coated on a quartz wafer and baked at 100 °C for 5 min. The UV absorption changes were monitored after the polymer film was exposed to a 254 nm light. The UV exposure was carried out with a Ushio Model UI-5010 equipped with a 400 W Hg lamp. The resist film was exposed to a collimated 254 nm light or a 365 nm light passed through a 254 nm filter (MIF-UW) or a 365 nm filter (UV35).

Contrast Curve. Polysilane in toluene was spin-coated on a quartz wafer and baked at 100 °C for 5 min. The UV exposure was carried out in the same way as described in the section Photolysis. After the exposure, the wafer was developed with a 2.38% TMAH aqueous solution at room temperature. The contrast curve was obtained by measuring the thickness of the resist film remaining after 1 min of development, when the dose was changed.

Determination of the Amount of Acids Photogenerated from EA1. The amount of carboxylic acids photogenerated from EA1 in polymer matrixes was determined by employing an acid indicator, tetrabromophenolblue sodium salts (AI), as follows.[38,39] EA1 (1.5 g) and polysilane **1** (10 g) were dissolved in 100 mL of toluene. The toluene solution was spin-coated on a Si wafer which had a 001 crystal surface. Then the wafer was baked at 100 °C for 5 min in order to remove toluene. The Si wafer was cut out to be 10 mm × 10 mm. Si wafers having the 001 crystal surface make the precise square cut possible because of cleavages along the crystal axis. Exposure was carried out with the same exposure apparatus as described in the Photolysis section. The amount of EA1 molecules in the polysilane on the Si wafer was calculated from the film thickness and the surface area. The cut Si wafer was dissolved in 3 mL of methyl 3-methoxypropionate in which 1.0×10^{-4} wt % of the acid indicator was dissolved. The indicator (AI) has a UV absorption at 602.5 nm which decreases in the presence of acid. The amount of photogenerated acids in the polymer matrix was estimated from the calibration curve which exhibits the relation between the amount of acids and the decrease in the UV absorption. 2-Benzophenone carboxylic acid was employed as the model compound of the photogenerated carboxylic acid. Namely, the amount of photogenerated carboxylic acids was converted to that of 2-benzophenonecarboxylic acid moieties.

Electrochemical Measurements.[40,41] All electrochemical measurements were carried out in a cell using a Pt working electrode, a Pt wire counter electrode, and a Ag reference electrode and using a Polarization Unity PS-07 (Toho Technical Research) potentiostat. The reduction and oxidation potentials were standardized with that of ferrocene. A solution containing 0.1 M Et_4NBF_4 and 10^{-3} M polysilanes or electron acceptors in THF or acetonitrile was employed. The concentration is based on the weight of the monomer unit. The solution was degassed with a slow stream of dry nitrogen. THF and acetonitrile were dried over molecular sieves. Polarographic oxidation waves for polysilanes were irreversible. Therefore, half-wave potentials quoted in this paper are estimated ones.

Fluorescence Quenching.[34,35] Measurements were carried out on a Hitachi F-300 spectrofluorometer. Front-face illumination of concentrated **1** solution was employed because of the photolability. Wallraff and co-workers have reported that the results obtained by this front-face illumination method using concentrated polysilane solutions were comparable to those obtained from experiments using dilute polymer solutions in a flow cell.[34,35] The quencher concentration had less than 1% UV absorption at the excitation wavelength (330 nm). The scan time was adjusted so that no photodegradation was observed in repetitive runs. Electron acceptors (quenchers) were added to 0.025 M poly(methylphenylsilane) in spectroscopic-grade THF, and the decrease in the fluorescence quenching of the poly(methylphenylsilane) was monitored.

Results and Discussion

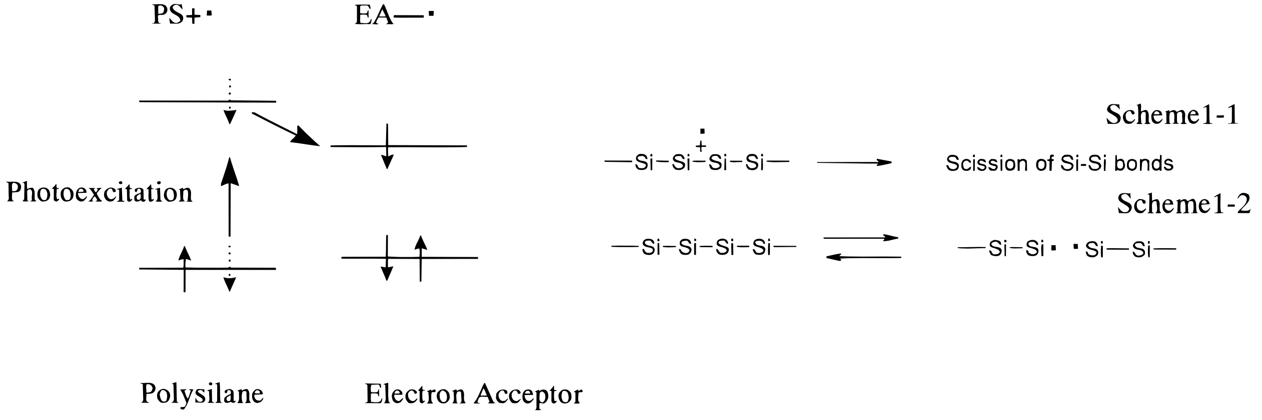
The sensitivities of polysilane resists are associated with both the photolysis rates of the polysilane and the dissolution rates of the photolysis products in a basic aqueous solution. In this paper, the photolysis rates and the dissolution rates are discussed individually.

1. Photolysis. Miller et al. have reported that electron transfers from photoexcited polysilanes to electron acceptors such as EA4, EA5, and EA7 in Figure 1 are responsible for the increase in the photolysis rate of polysilanes.[8,15,34,35] The resultant polysilane radical cations cause cleavages of Si–Si bonds, which should be much more efficient than homolytic cleavages of Si–Si bonds in the absence of these electron acceptors, because radical recombination has to be considered in the latter process (Scheme 1-2).

They concluded that the photosensitization is caused by photoinduced electron transfers because (1) the fluorescence quenching of poly(methylphenylsilane) is a function of the reduction potential of the additive, (2) reactions with larger exothermic values for free energy changes tend to have larger fluorescence quenching rates, and (3) the kinetics of quenching is described by the Stern–Volmer formalism.[34,35] We followed the same procedure as that in these reports in order to elucidate the increase in the photolysis rates of polysilane **1** in the presence of EA1.

1.1. Relations between Reduction Potentials of Electron Acceptors and Polysilanes. Figure 2 summarizes oxidation and reduction potentials for polysilanes and electron acceptors. EA1 has two moieties which are electrochemically active, namely, a benzophenone moiety and a peroxide moiety. Therefore, EA1 was compared with benzophenone and dibenzoylperoxide.

Scheme 1. Photoinduced Electron Transfer from Photoexcited Polysilane to Electron Acceptor



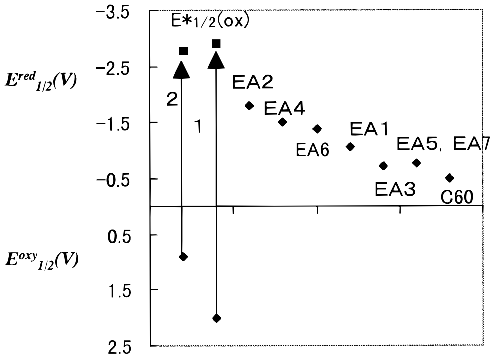


Figure 2. Oxidation and reduction potentials of polysilanes and electron acceptors: EA1, EA2, and EA6, this study; EA3, EA4, EA5, and EA7; refs 34 and 35; $E^*_{(1/2)}(\mathrm{ox}) = E^{\mathrm{oxy}}(1/2) - E(0,0)$; $E^{\mathrm{oxy}}(1/2)$, estimated half-wave oxidation potential; $E(0,0)$, excitation energy of the polymer (eV).

EA1 was also compared with representative electron acceptors reported in previous papers.[34,35]

Fluorescence quenching experiments were carried out by employing **2** instead of **1**, because the fluorescence from **1** is weak. The weak fluorescence is probably due to the low molecular weight of **1**. The presence of contaminant quenchers may decrease the fluorescence effectively because of the low molecular weight. $E^*_{(1/2)}(\mathrm{ox})$ of **1**, which corresponds to the LUMO, is almost the same as that of **2**, where $E^*_{(1/2)}(\mathrm{ox})$ is defined as follows:

$$E^*_{(1/2)}(\mathrm{ox}) = E^{\mathrm{oxy}}_{(1/2)} - E(0,0)$$

where $E^{\mathrm{oxy}}_{(1/2)}$ is the estimated half-wave oxidation potential and $E(0,0)$ is the excitation energy of the polymer (eV). Therefore, the fluorescence quenching experiment for **2** should be valid in order to elucidate the photoinduced electron transfer of **1**. The $E^{\mathrm{red}}_{(1/2)}$ values from EA1 to EA7 were lower than the $E^*_{(1/2)}(\mathrm{ox})$ values of **2** and decreased as follows: EA2 > EA4 > EA1 > EA5 = EA7 > EA3.

The free energy change of photoinduced electron transfer ΔE_{ET} is defined as follows, according to the Rehm−Weller equation:[42,43]

$$\Delta E_{\mathrm{ET}}\ (\mathrm{kcal/mol}) = 23.06(E^*_{(1/2)}(\mathrm{ox}) - E^{\mathrm{red}}_{(1/2)}) - e_0^{\,2}/a\epsilon$$

where $E^{\mathrm{red}}_{(1/2)}$ is the reduction potential of electron acceptor and $e_0^{\,2}/a\epsilon$ is the Coulombic energy term for THF in this experiment, where this term is omitted because of the relatively low dielectric constant of THF.

Table 2. Fluorescence Quenching of 2 with Electron Acceptors

electron acceptor	ΔE_{ET} (kcal/mol)	K_q ($\times 10^{-10}$ M^{-1} s^{-1})
EA2	−22	212
EA4	−30	17
EA1	−39	221
EA5	−46	12
EA7	−41	20
EA6	−32	6
EA3	−48	12

Fluorescence quenching was analyzed by employing Stern−Volmer kinetics, which is often followed by purely diffusional quenching of fluorescent materials by electron acceptors.[44]

$$F_0/F = 1 + K_{\mathrm{SV}}[\mathrm{Q}]$$

$$K_{\mathrm{SV}} = K_{\mathrm{q}}(\tau_0)$$

where K_q is the bimolecular quenching constant, (τ_0) is the fluorescence lifetime of poly(methylphenylsilane), 86 ps,[34,35] [Q] is the electron acceptor concentration, F_0 is the fluorescence in the absence of electron acceptor, and F is the fluorescence in the presence of electron acceptor.

Figure 3 shows the relation between F_0/F and the electron acceptor concentration. The Stern−Volmer plot shows slightly positive deviation from linearity at higher acceptor concentration. Therefore, we fitted it at low acceptor concentration by using the method of least squares in order to obtain Ksv and K_q. Figure 3 clearly shows that **2** is quenched much more efficiently by the addition of EA1 and EA2, compared to other electron acceptors.

Table 2 summarizes ΔE_{ET} and K_q. The data reported by Miller et al. are also described. The values on reduction potential and K_q for EA5 we obtained were almost the same as those reported by Miller et al. Therefore, the comparison of our data with the published data should be valid.[34,35] It has been reported that a typical diffusion-controlled bimolecular quenching constant for small molecules diffusing in toluene at room temperature is 1.1×10^{10} M^{-1} s^{-1} and the larger quenching constants for poly(methylphenylsilane), 10−20 $\times 10^{10}$ M^{-1} s^{-1}, than expected are explained by rapid energy migrations along the polysilane chains.[34,35] This may be explained by exciton transports along the polysilane backbone, since polysilanes have been known to have excitonic excited states.[45] Table 2 shows that EA2 and EA1 have one order larger K_q values than other electron acceptors reported,[34,35] even when ΔE_{ET}

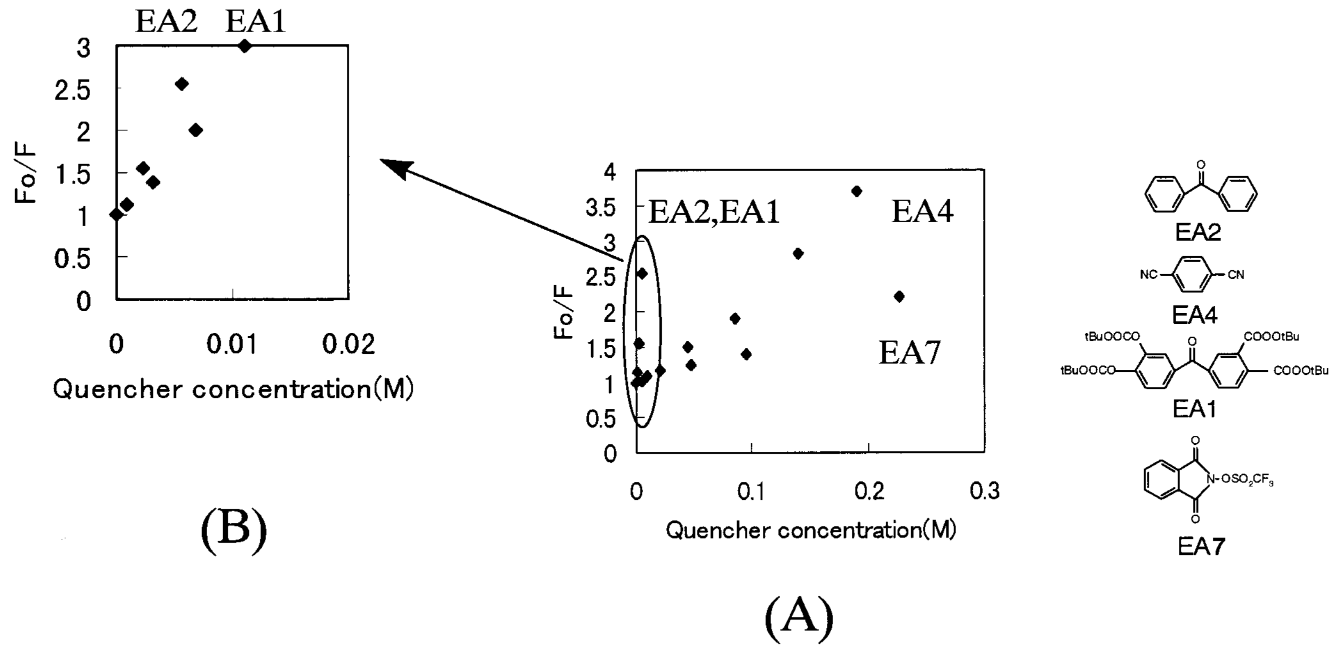


Figure 3. Relation between F_0/F and electron acceptor concentration [Q] (Stern–Volmer plot fitting). Polysilane **2** was excited with a 330 nm light, and the fluorescence was monitored at 357 nm. In part B, the horizontal line (electron acceptor concentration) is expanded. EA1, EA2, and EA7, this study; EA4, refs 34 and 35.

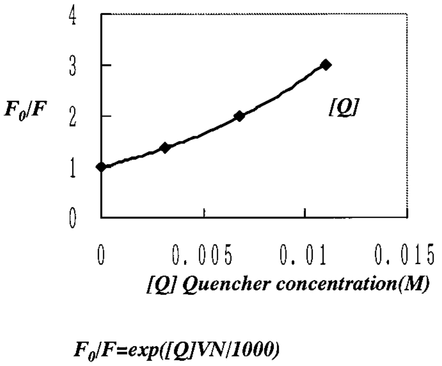


Figure 4. Relation between F_0/F and electron acceptor concentration [Q] (Perrin fitting). Polysilane **2** was excited with a 330 nm light, and the fluorescence was monitored at 357 nm. Electron acceptor, EA1.

for EA1 is smallest and ΔE_{ET} for EA2 is comparable to that for EA7, which is in an intermediate ΔE_{ET} among those of the electron acceptors listed in Table 2.

Contrary to Stern–Volmer kinetics, which takes diffusions of fluorescent materials into account, Perrin active sphere quenching premises that all molecules contained within the active sphere instantaneously quench the excitation without diffusion. In this situation, the quenching kinetics is described as follows:[46]

$$F_0/F = \exp([Q]vN/1000)$$

where v is the active quenching volume and N is Avogadro's number.

The fluorescence quenching of **2** in the presence of EA1 fitted the Perrin formalism better than the Stern–Volmer fitting, as shown in Figure 4, and the active sphere volume was calibrated to be 1.63×10^{11} Å^3 (radius 3400 Å). The value is too large, because perchloropentacyclododecane has been reported to quench the fluorescence of **2** with the v value 10 000 Å^3 (radius 13 Å).[34,35] We have reported that photoinduced electron transfers from polysilane LB films to photoexcited TCNQ LB films did not occur over a distance of 50 Å when polyacrylate LB films were incorporated between the polysilane LB film and the TCNQ LB film.[47]

Let us presume why EA1 and EA2 show anomalous behavior for fluorescence quenching of polysilane **2**, compared with those of other additives previously reported.[34,35]

There are a few reports on photosensitizations of peroxides. When EA1 was exposed to UV lights, homolytic cleavages of peroxide moieties occurred, followed by fast decaroxylation reactions via the photoexcited triplet state to form phenyl radical derivatives.[48–52] Savary et al. have reported that sensitization of thiopyrylium salt occurs via energy transfer from the triplet of the thiopyrylium salt to the triplet of EA1.[53] EA1 has been reported to be sensitized by electron transfers from photoexcited coumarin dyes and thioxanthene dyes to **2**.[54]

Photosensitization of dibenzoylperoxide in the presence of aromatic compounds has been explained by exciplex formation in singlet sensitization and excitation transfer to peroxide molecules in a vibrationally hot ground state in singlet and triplet sensitizations.[55,56] Namely, photosensitization of peroxides has been explained by electron transfers, singlet and triplet energy transfers, and exciplex formations.

The possibility of the energy transfer would be denied because of the following reasons. EA1 and EA2 have weak UV absorptions at 338 nm (log ϵ:2.23) and 350 nm (log ϵ:2.08) in chloroform, respectively.[50] Needless to say, these UV absorptions added for the fluorescence quenching are very small and negligible. **2** has a fluorescence at 357 nm. In the case of EA2, there is no overlap of the UV absorption of EA2 and the fluorescence of **2**. Therefore, Förster type energy transfer is not likely. The overlap seems to be observed in case of **2** and EA1. However, if this fluorescence quenching is caused by energy transfers from photoexcited polysilanes to EA1, the acceleration of the polysilane photoscission must not be observed, because energy transfers

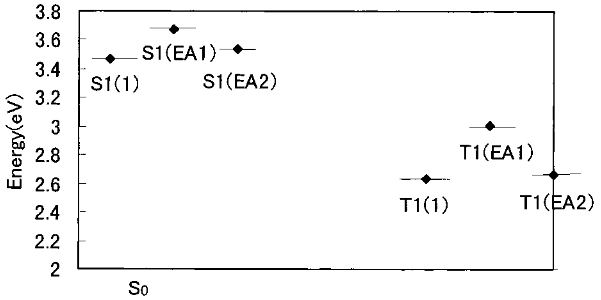


Figure 5. Energy diagram of **1**, EA1, and EA2: **1**, ref 57; EA1, ref 65; EA2, ref 58.

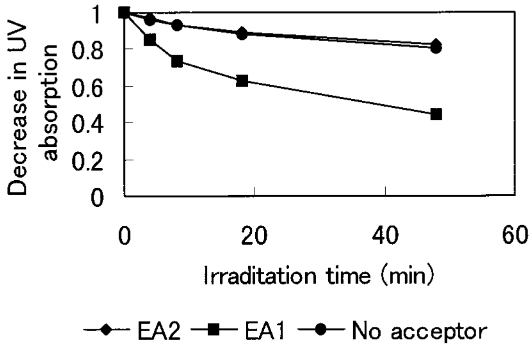


Figure 6. Decrease in UV absorption of polysilane **2**: UV exposure, 365 nm; observation, 340 nm.

mean only the quenching of the photoexcited polysilanes. For the same reason, triplet energy transfers from **2** (2.64 eV, triplet)[57] to EA2 (3.01 eV, triplet)[58] would be also denied. These energy diagrams are summarized in Figure 5.

No difference in UV absorption and emissions for **2** was observed after EA1 and EA2 were added to a solution of **2**, which implies that EA1 and EA2 do not make quantitative ground-state charge transfer complexes nor excimer complexes with **2**. The anomalous fluorescence quenching is not observed for dibenzoylperoxide (EA3). Therefore, the excitation transfer to peroxide moieties in a vibrationally hot ground state would be also denied.[55,56] In this stage, we do not exclude the possibility of weak, partial formation of these complexes. However, we tentatively attribute this phenomenon to weak interactions such as hydrophobic interactions between a benzophenone structure and polysilane substituents or hydrophilic interactions between a benzophenone carbonyl and Si–OH's of the polysilane chain ends. If we assume that EA1 may locate close to polysilanes with configurations suitable for electron transfers by the weak interaction,[59] the fact that electrons shift effectively from photoexcited polysilanes to EA1 and EA2 should be explained well. The interaction should occur at the benzophenone moiety of EA1 because dibenzoyl peroxide (EA3) does not quench the polysilane as much as EA2 does.

1.2. Photobleaching of Polysilanes in the Presence of EA1 and EA2. The fluorescence quenching rates of **2** in the presence of EA1 were almost the same as those in the presence of EA2. Because of the photoinduced electron transfer reaction, EA1 actually increased the photolysis rate of poly(methylphenylsilane). However, EA2 did not. Figure 6 shows the differences clearly. The same phenomena were seen when **1** or **2** was exposed to a 254 nm light in the presence of EA1 or EA2.

The comparison of EA1 with EA2 provides a look at the mechanism of the acceleration of polysilane photolysis in the presence of electron acceptors. When polysilanes are photoexcited, electrons shift from polysilanes to acceptors to form polysilane radical cations and acceptor radical anions. The radical anion should exist as a counteranion of the polysilane radical cation. Radical anions of EA1 have peroxide moieties and should decompose to carboxylate anions and *tert*-butyloxy radicals. Therefore, the electron does not get back to the polysilane radical cation, leading to Si–Si bond cleavages of the polysilane radical cation, where nucleophilic attacks may be needed from the viewpoint of the energy diagram, as will be discussed later. However, in case of EA2, because the EA2 radical anion should be very stable, the polysilane radical anion would have a chance to obtain an electron from the (EA2) radical anion to form the parent polysilane by back-electron transfers.

Tentative MO calculation (PM3) results are summarized in Figure 7, where the model compounds shown were employed and counterions were omitted for simplicity. When $PhCOOOCH_3$ received an electron to form $PhCOOOCH_3^{\bullet -}$ (M1), the radical cation decomposed to form $PhCOO^-$ (M1-1) and $MeO^\bullet$ (M1-2) which are energetically preferable to the formation of $PhCOO^\bullet$ (M1-3) and MeO^- (M1-4). The difference in the heat of formation between M1 and M1-1 + M1-2 is only a few kilocalories per mole. On the contrary, the heat of formation of M2-1 + M2-2 or M2-3 + M2-4 was much higher than that of M2. The same results were obtained when $Me(SiPhH)_4Me$ was employed as the model compound. This implies that it is not likely that polysilane radical cations photodecompose spontaneously to form the silyl radical species and silyl cations. Probably, nucleophilic attacks by COO^-, which should be close to the polysilane radical cations, may help the Si–Si bond cleave.

In the course of this study, we found that **2** was strongly quenched by C60. The bimolecular quenching rate K_q was 300 times larger than that of EA1. It has been reported that photoinduced electron transfers actually occur from photoexcited polysilanes to C-60.[60,61] The fluorescence of polysilane films has been reported to be quenched in the presence of C-60, where the quenching rates have not been compared with those of other electron acceptors.[62] When **2** or **1** was exposed to a 254 nm light in the presence of C-60 (0.5 wt % to polysilanes), we found that the photolysis rate actually decreased, compared with that in the absence of C-60. This may be another case of EA2; namely, back-electron transfers occur from very stable C-60 radical anions to polysilane radical cations. The C-60 radical anion has been reported to survive for more than 1.5 s.[63] Recently it was reported that the photoscission of polysilane in the film was reduced in the presence of C-60 without any comparison with other electron acceptors.[64]

Miller and co-workers have reported that the photolysis of poly(methylphenylsilane) was slowed in the presence of perchloropentacyclododecane in spite of the fact that effective fluorescence quenching of poly(methylphenylsilane) was observed in the presence of perchloropentacyclododecane. They implied that this may be due to rapid back-electron transfer.[34,35] Our results on EA1, EA2, and C60 clearly support this. The photolysis rates of **1** increased in the presence of EA1, EA5, and EA7. They have a labile bond which acts like

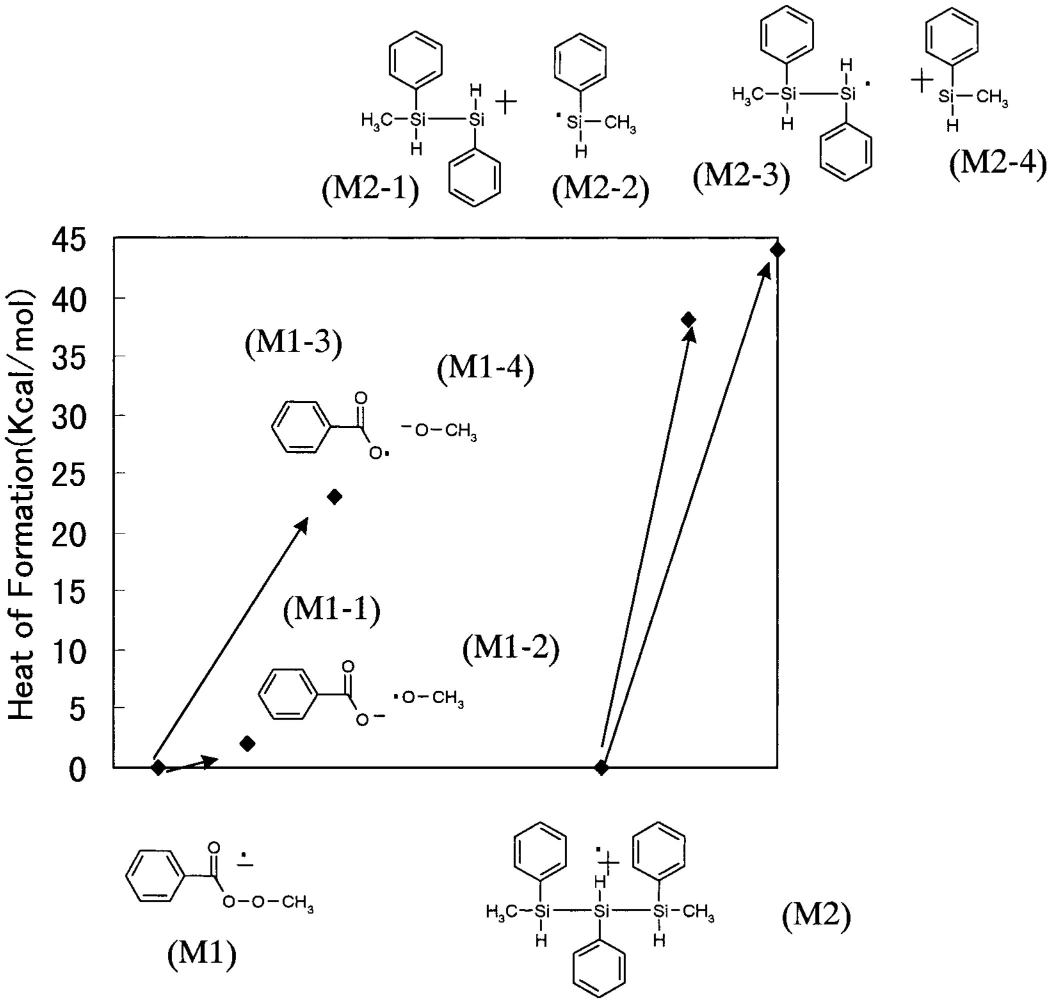


Figure 7. Tentative energy (heat of formation) calculation on O–O and Si–Si scission of radical anion and radical cation. The perpendicular line shows the relative heat of formation when the heat of formation of M1 and M2 was 0 kcal/mol.

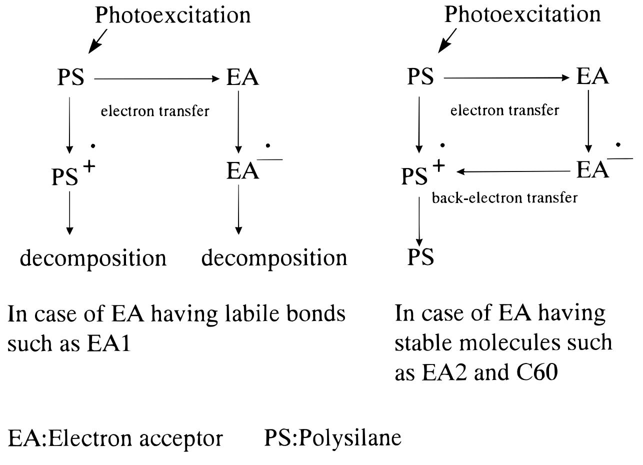


Figure 8. Comparison of two types of electron acceptors for photoinduced electron transfer from polysilane.

nucleophiles such as CCl_3 and $NOSO_2CF_3$. On the other hand, the photolysis rates decreased in the presence of perchloropentacyclododecane, EA2, and C-60. We concluded that, in order to increase polysilane photolysis rates, electron acceptors need labile bonds to cleave. The difference is summarized in Figure 8.

2. Development. 2.1. Acid Generation. It has been reported that peroxy moieties of EA1 photodecompose homolytically to form *tert*-butyloxy radicals and carboxylic radicals which further decompose to form phenyl radicals.[49-52]

Some reports were seen on photodecomposition products of benzoylperoxide (BPO) in the presence of aromatic photosensitizers. In the case of direct photolysis of BPO, $PhCO_2Ph$ (a cage product), Ph-Ph, and Ph-COOH were observed, and the ratio was 16%:55%: 28%.[55] In the presence of aromatic photosensitizers, the amount of PhCOOH molecules in the photolysis products was extremely high in the presence of perylene, compared with that in the presence of other photosensitizers, such as naphthalene, triphenylene, and anthracene. However, an explanation of the large amount of PhCOOH was not given in that paper. Addition reaction products of naththalene (sensitizer) with BPO were also separated.[59] These reports prompted us to compare the amount of carboxylic acids formed from EA1 in the presence of **2** with that formed in the absence of **2**.

When photoinduced electron transfers from polysilane to EA1 form a radical anion of EA1, the radical anion should give carboxylate anions and *tert*-butyloxy radicals, as was speculated from our MO calculation (Figure 7). Therefore, the amount of carboxylic acid in the latter case should be larger than that in the former case. The amount of carboxylic acid was determined by titration after EA1 was fully photodecomposed in a film of **1** and a poly(methyl methacrylate) film, respectively. The

Table 3. Amount of Carboxylic Acids from EA1

run	polymer	additive	acid detected[b] ($\times 10^7$ mol)
1[a]	polysilane **1**	EA1	5.3
2[a]	polysilane **2**	EA1	6.2
3	PMMA	EA1	2.7
4	polysilane **1**		1.3
5	polysilane **2**		1.3
6	$Ph_2Si(OH)_2$		0

[a] In the case of runs 1 and 2, these data are corrected with runs 4 and 5. [b] The amount of acid is calibrated with 2-benzophenonecarboxylic acid. There is 8.4 × 10^{-7} mol of EA1 in the cut polymer film.

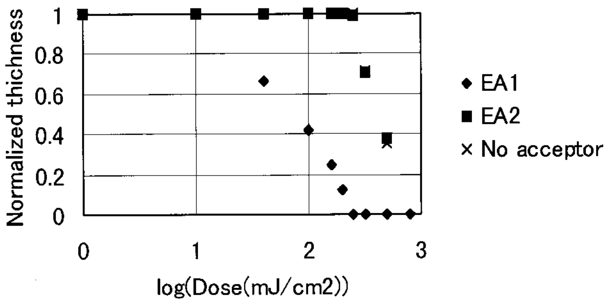


Figure 9. Contrast curves of polysilane resist **1** in the presence of EA1 and EA2: exposure, 254 nm light; development, 2.38% tetramethylammonium hydroxide aqueous solution for 1 min.

photolysis products from **2** have not been determined so far.

The amount of carboxylic acids formed from EA1 in a poly(methylphenylsilane) film was twice as large as that in a poly(methyl methacrylate) film, as shown in Table 3. Photolysis products from **1** or **2** decreased the UV absorption of the acid indicator (AI), as is shown in runs 4 and 5, probably because aggregations of SiOH's bonded to oligomeric photolysis products make acid sites. Monomeric diphenylsilanediol did not change the UV absorption of AI. Therefore, runs 1 and 2 have been corrected with data from run 4 or 5. This is also explained well by the photoinduced electron transfer from polysilane to **2**.

2.2. Development in the Presence of Carboxylic Acid Derivatives. When **1** was exposed to a 254 nm light, **1** photodecomposed to form silanols bearing phenyl groups which are soluble in dilute basic aqueous solutions. This is why **1** is developed with aqueous solutions after the photoexposure. **1** did not dissolve in basic aqueous solutions at all. However, when only 5 wt % of a model compound, 2-benzophenonecarboxylic acid, is added to **1** without any UV irradiation, the dissolution rate increased to 250 nm/min in a 2.38% tetramethylammonium hydroxide solution. Considering the fact that the dissolution rate was 550 nm/min when **1** was fully exposed to a 245 nm light, photolysis products bearing carboxylic acids would have an important role for accelerating the resist sensitivity.

In this sense, an electron transfer from photoinduced polysilanes to **1** serves to increase both photolysis rates and dissolution rates.

2.3. Contrast Curves for 1 in the Presence of EA1 and EA2. Figure 9 shows contrast curves of polysilane resists containing **1** in the presence of EA1 or EA2, when a 254 nm light was exposed. It is clear that EA1 increased the resist sensitivity, but EA2 did not do that at all, in spite of the fact that the fluorescence quenching rate of **2** in the presence of EA1 was almost the same as that in the presence of EA2. The shape of the contrast curves implies that **1** undergoes cross-linkings as well as pure scissions. It has been reported that both scission and cross-linking occur when poly(phenylmethylsilane) was photodecomposed.[3,37,66,67] This should be the case for **1** bearing phenyl groups, because the cross-linking has been attributed to the reaction of phenyl groups with silyl groups. The decrease in the cross-linking reaction is the next issue to be solved in order to obtain a high γ value, namely high contrast patterns.

2.4. Total Reaction Mechanism. The proposed mechanisms for increases in the sensitivity of polysilane resist **1** in the presence of EA1 are as follows: Electrons shift from photoexcited polysilane **1** to EA1 to form radical cations of **1** and radical anions of EA1. The radical anions of EA1 decompose to form benzophenone derivatives bearing carboxylic acids. The radical cations of **1** decompose to form polysilanes bearing phenylsilanols accompanied by decreases in the molecular weight. Both benzophenone derivatives bearing carboxylic acids and phenylsilanols are responsible for the dissolution in basic aqueous solutions and the increase in the resist sensitivity.

Conclusion

The mechanism of the increase in the resist sensitivity of **1** in the presence of EA1 was described. EA1 increases both the photolysis rates and the dissolution rates in a basic aqueous solution. The increase in the photolysis rates was explained by efficient photoinduced electron-transfer reactions from photoexcited polysilanes to EA1, followed by the decomposition of the peroxide moieties. This prevented the electrons from getting back to the polysilane radical cations. Products formed from EA1 by photoinduced electron transfers are aromatic compounds bearing carboxylic acids which promote the dissolution rates in a basic aqueous solution. The comparison of EA1 with benzophenone and C-60 implied that electron acceptors bearing labile bonds accelerate photodegradations of polysilanes and that the presence of peroxides was crucial.

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