Application of Polysilanes to LSI Manufacturing Processes—Their Antireflective Properties and Etching Selectivity toward Resists

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Fundamental aspects for a novel LSI pattern fabrication process employing polysilanes as an antireflective layer (ARL) are discussed. The multilayer is composed of an organic resist, a polysilane layer, and a substrate. The polysilane avoids reflections from the substrate when the resist is exposed to 248-nm light emitted from a KrF excimer laser. It also acts as a pattern transfer layer. The polysilane layer is etched faster than the resist when the etching is carried out with reactive ions by employing Cl_2 gas. Therefore, the resist pattern is transferred to the polysilane layer precisely. The relationship between the structure of the polysilane and its physical properties, namely, the UV absorbance at 248 nm and etching selectivity toward the organic resist, is discussed and the best polysilane structure for this application identified.

1. Introduction

Deep UV exposure tools now allow the printing of feature sizes down to 0.20 μm, though difficulties are typically encountered using single-layer resist processes in applications involving topography and reflective substrates. The conventional process using a polymer layer containing silicon atoms on an organic polymer base layer provides a solution to the problem. The top layer acts as the photoimaging layer and a hard mask for the etching of the underlying substrate. The bottom layer acts as an antireflective layer as shown in Figure 1. One of the silicon-containing polymers, polysilane, has been investigated extensively as the photosensitive top layer.[1−28]

Their unique photoreactivity and high silicon content, facilitating excellent pattern transfer, make polysilanes ideally suited for this process. The pattern of the

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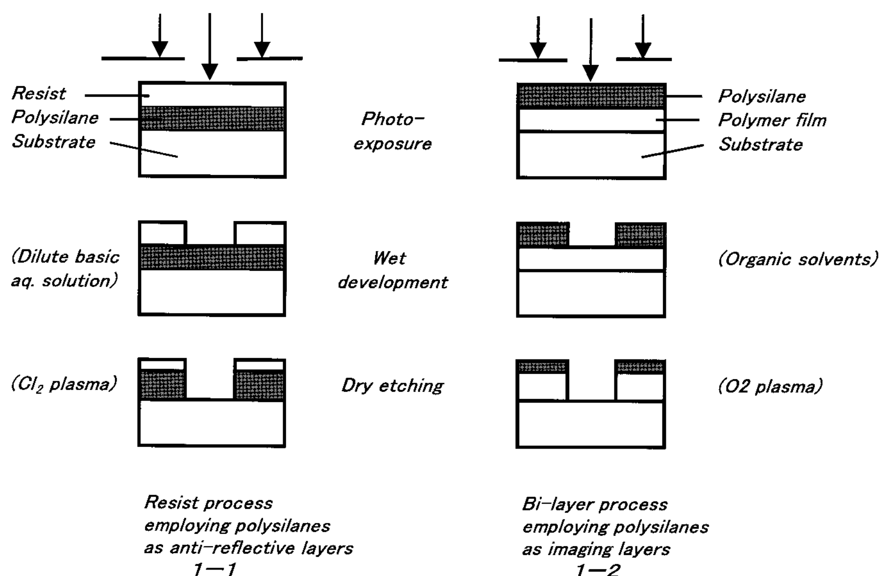

Figure 1. Difference between the polysilane bilayer resist process and polysilane antireflective layer process.

polysilane layer is fabricated by its exposure to deep UV light, followed by wet development. Then, the organic polymer layer under the polysilane layer is etched with oxygen-reactive ions (O_2-RIE). In this process a SiO_2 layer formed at the surface of the polysilane during the O_2-RIE acts as the hard mask for the etching of the underlying substrate. This process has high potential. However, to date, the profile of polysilane patterns fabricated by wet development techniques, employing the basic aqueous solutions in current commercial use, has not reached the level required.[24−28]

A novel process employing dry developments has been reported to generate high-resolution patterns. This dry development is carried out using Cl_2 or HBr gas. The unexposed polysilane area is etched faster than the photooxidized polysilane, providing the negative image.[9,11,12,15,17] The highly cross-linked polymethylsilane film prepared by a chemical vapor deposition process (CVD process) has been reported to provide a high-resolution pattern. However, the handling of the film is not easy because the film is easily oxidized in an ambient atmosphere.

We would like to propose another potential use of polysilanes for ULSI fabrication, where the polysilane acts as an antireflective layer (ARL) as well as a hard mask for fabricating underlying substrates. The multilayer is composed of a resist layer, a polysilane layer, and a substrate, as shown in Figure 1. Preventing reflections from the substrate is crucial for deep UV lithography employing KrF (248 nm) and ArF (193 nm) excimer lasers.[29−31] An organic resist is spin-coated on a polysilane layer and exposed to UV lights through photomasks. The polysilane layer absorbs the UV light passing through the resist layer and prevents reflections from the underlying substrate. After the resist pattern is fabricated, the multilayer is exposed to Cl_2 plasma. Because the polysilane layer, consisting of consecutive Si−Si bonds, is etched faster than the resist layer, the resist profile is transferred exactly to the polysilane layer. This process has two advantages. First, high-resolution organic resists can be used freely, without the synthetic limitations experienced when using silicon-containing resists. Second, the thickness of the resist for this process can be thinner than that for a single-layer resist process, which improves the process latitude during exposure. Antireflective properties are attainable by employing conventional organic polymers not bearing silicon atoms. However, it is difficult to etch the organic antireflective layer selectively using the resist mask because both the antireflective polymer and the resist polymer have aliphatic hydrocarbon structures.

To complete the ARL process successfully, a number of features are important, for example, the solubility properties of the polysilane as it is necessary to prevent the polysilane layer from mixing with the resist layer. We require the ability to make a planar film, high glass transition temperatures (T_g), antireflective properties, a high etching selectivity toward resists, and a high etching durability toward underlying substrates. In this paper, we focuses on clarifying the relationships between the polysilane structure and the etching selectivity toward the resist and the polysilane structure and its UV absorbance at 248 nm.

Our goal is to find the polysilane structure with a UV absorbance at 248 nm greater than 0.8 (0.1-μm thickness) and an etching selectivity toward the resist of greater than 2.0.

2. Experiment

2.1. Material. Polymer structures used in this study are summarized in Figure 2.

All solvents employed for syntheses were dried before use. All syntheses were carried out under an Ar atmosphere. Poly(phenylhydrosilane), P1, was synthesized according to the method reported by Li et al.[32] Other polysilanes were prepared by the Wurtz coupling reaction.[33] These corresponding di-

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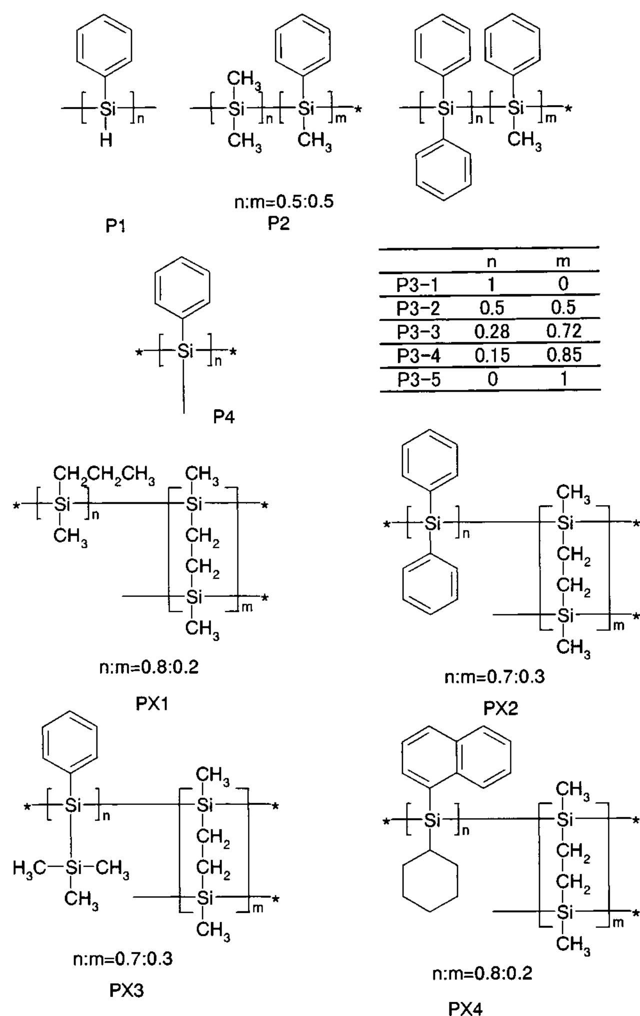

Figure 2. Polysilane structures and their abbreviations.

chlorosilanes and 1,2-bis(dichloromethyl)ethane were employed for the syntheses of PX1, PX2, PX3, and PX4.

2.2. Syntheses and Characterizations for New Polysilanes. Caution: Na dispersion is very sensitive toward moisture and air. During syntheses, the reaction vessel must be maintained under inert conditions. *CAUTION: Danger of Explosion!* Monomers should be added slowly to the reaction mixture under controlled conditions so as to maintain gentle reflux. Care should be taken especially at the beginning of the addition as the reaction has an induction period.

In a four-necked round-bottomed flask equipped with a dropping funnel and a condenser, 130 ml of xylene, 20 ml of anisol, 0.35 g of CuCl, and 20.6 g of Na were placed. The sodium was dispersed by stirring the mixture vigorously at 120 °C. Then, diphenyldichlorosilane (63.38 g, 0.25 mol) and 1,2-bis(dichloromethylsilyl)ethane (15.37 g, 0.06mol) were added for 20 min and stirred for 2 h at 120 °C. After the reaction mixture was cooled down to room temperature, 500 ml of toluene was added. After the precipitate was removed under an Ar atmosphere, the solvent in the filtrate was removed under a reduced pressure. The residue was again dissolved in 100 ml of toluene. Then, the polysilane was precipitated from 500 ml of ethyl lactate. The polymer was purified three times in the same manner and dried at 90 °C for 1 day. PX2: Yield 33%. ^{1}H NMR (270 MHz $CDCl_3$) δ (ppm): 0 (SiMe, broad), 1.0 (Si−CH_2−, broad), 7.1 (Si−Ph, broad). IR(KBr) (cm^{-1}): 3150, 2980, 1420, 1110, 780, 750, 710. M_w 13 000. Other polysilanes were synthesized in a similar way.

PX-1: NMR ($CDCl_3$) δ (ppm), 0.5 (SiMe, broad), 1.0 (Si−CH_2−, C−CH_3, broad), 1.4 (C−CH_2−C, broad); M_w 16 000. PX-3: NMR ($CDCl_3$) δ (ppm), 0 (SiMe, broad), 1.0 (Si−CH_2−, broad), 7.0 (Si−Ph, broad); M_w 8 000. PX-4: NMR ($CDCl_3$) δ (ppm), 0−2.0 (cyclohexyl, SiMe, Si−CH_2−, broad), 7.0 (Si−Naph, broad); M_w 4 300.

The T_g's of P2, P3−2, P3−3, P3−4, P3−5, and PX2 were 61, 128, 120, 122, 81, and 155 °C, respectively. The T_g's of other polysilanes were not measured. All polysilanes prepared were soluble in toluene and xylene.

2.3. Preparation of Polysilane Films. After a polymer in toluene solution was spin-coated on a substrate, the substrate was baked at 190 °C for 1 min under an Ar atmosphere. The UV absorption of P1 having hydrogen groups decreased when the film was baked at 190 °C in air. Polysilanes except for P1 were stable in air.

2.4. Preparation of Resist Patterns. The chemically amplified positive resist (R1), which has polyvinyl phenol structures, was employed in this study. After being coated, the film was baked at 100 °C for 90 s to evaporate these solvents. Then, the film was exposed to 248-nm light and then baked at 100 °C for 90 s. The resist was developed with a 2.38% tetramethylammonium hydroxide aqueous solution for 1 min. A scanner equipped with a KrF excimer laser (NA, 0.6, σ, 0.75) was employed for the exposure. To evaluate the resist pattern, mixing of the resist and polysilane layers should be avoided. Further discussion of the mixing layer will be reported elsewhere. The polysilane, which is insoluble in ethyl lactate, used for the resist solvent was selected for the pattern fabrication.

2.5. Dry Etching. The etching rate for the resist and the polysilane was monitored in reactive ion etchers. The etching was carried out at 80 °C by employing Cl_2 gas.

2.6. UV Absorption. UV absorption was recorded with a Shimazu Model UV-260 visible recording spectrometer. Refractive indexes were measured with a Sorpra ellipsometer. Polysilanes were coated on a quartz plate and baked in the same matter described in the section Preparation of Polysilane Films.

2.7. Characterization of Polymer Films. X-ray photoelectron spectroscopy (XPS) was recorded with a ULVACΦ model Quantum 2000. Decomposition products were analyzed by a MS apparatus equipped with a MS(HP5972A) MS selective detector. NMR spectra were recorded with a JEOL model GSX-270 spectrometer. IR spectra were recorded with a Nippon Bunko model FT-IRWS/IR-8300.

3. Results and Discussion

3.1. UV Absorption. Antireflective properties of polysilanes were compared to each other by measuring the UV absorbance of their films with 0.1-μm thickness. The UV absorbance was monitored at 248 nm, the wavelength employed for KrF excimer laser lithography. Details for the antireflective property of polysilanes should be reported elsewhere.[34]

Linear polysilanes have unique UV absorptions in the region from 300 to 400 nm assigned to $\sigma-\sigma^*$ transitions. These UV absorptions vary, depending on the substituents on silicone atoms, the main chain conformation, the branching of the main chain, and molecular weights.[35−49]

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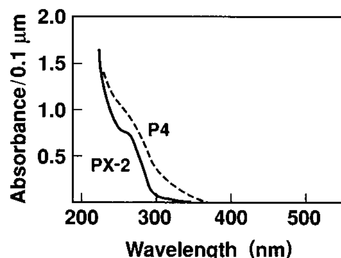

Figure 3. UV spectra for PX2 and P4. UV absorption was converted to 0.1-μm thickness.

The introduction of phenyl substituents on silicon atoms has been reported to shift the UV absorption peak up to around 400 nm and to increase the UV absorbance at around 250−300 nm assigned to the $\pi-\pi^*$ transition of the phenyl group.[33−39,43] The distortion of the silicon main chains disturbs the overlap of the silicon σ orbital and shifts the UV absorption peak to shorter wavelengths.[40−42] The branching of the silicon main chain and the decrease in the number of the consecutive silicon atoms also shift the UV absorption peak to shorter wavelengths.[35−39,44−49] $Me(SiMe_2)_5Me$ has a UV absorption peak at 250 nm. However, it was difficult to make the high-quality flat film with the polydimethylsilane oligomers. Therefore, the introduction of aromatic substituents, branched structures, and distorted structures was taken into account to increase the UV absorbance at 248 nm.

We synthesized three kinds of polysilanes. The P2 and P3 series are linear polysilanes substituted with phenyl groups. P1 and P4 have branched structures. We aimed at introducing the distorted structure by cross-linking the backbone with ethylene units such as PX1, PX2, PX3, and PX4 in Figure 2.

UV absorption peaks assigned to the silicon $\sigma-\sigma^*$ transition were clearly observed for P2, P3−1, P3−2, P3−3, P3−4, and P3−5[33] at around 300−400 nm, but those for P1, P4, PX1, PX2, PX3, and PX4 were observed as shoulders or were overlapped with other UV absorptions at around 250−300 nm. Representative UV absorption spectra for PX2 and P4 are shown in Figure 3. These spectra imply that the introduction of the branching and the chain distortion is effective for the increase in the UV absorption at 248 nm.

To examine the effect of the aromatic group, the UV absorbance for polysilane films with 0.1-μm thickness at 248 nm was plotted against the percentage of the aromatic group (Figure 4). In the case of methylphenylsilane−diphenylsilane copolymers (P3 series), the UV absorbance at 248 nm increased with increasing the percentage of the phenyl group.

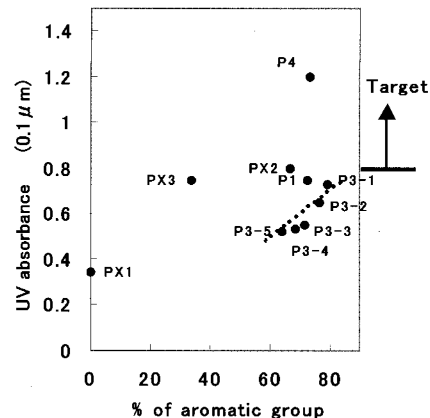

Figure 4. Relationship between UV absorbance and % of aromatic group. UV absorption was converted to 0.1-μm thickness. % of aromatic groups: wt %.

The UV absorbance of polysilanes cross-linked at the ethylene group (PX1, PX2, and PX3) was found to be higher than that of linear polysilanes, suggesting that partial cross-linking increases UV absorbance at 248 nm. The UV absorbance increased in the order of PX1, PX3, and PX2. PX3 had almost the same UV absorbance with PX2, even though the percentage of the phenyl group of PX3 (35%) was much less than that of PX2 (65%). The introduction of the silicon branched structure in PX3 may well explain the increase in the UV absorbance.

P4, having highly branched silicon backbones, has higher UV absorption at 248 nm than these linear polysilanes. The UV absorbance of P4 was higher than that of P1 having lower branched silicon backbones even though the percentage of the phenyl group of P1 is the same as that of P4.[44−47,49] Hydrogen atoms of P1 have been reported to be partially removed to make lower branched silicon backbones during the synthesis. This suggests that the silicon branched structure is also effective for the increase in the UV absorbance.

The intensity reflectance, R, is defined by the following equation,[50]

$$R = ((n_r - n_p)^2 + (k_r - k_p)^2)/((n_r + n_p)^2 + (k_r + k_p)^2)$$

where n_r is the refractive index of the resist, n_p is the extinction coefficient of the resist, k_r is the refractive index of polysilane, and k_p is the extinction coefficient of polysilane.

This equation shows that R decreases when n_r is close to n_p and k_r is close to k_p. R also decreases when n_r, n_p, k_r, and k_p have large values.

Figure 5 shows the relationship between the weight percentage of phenyl groups and n and k values for methylphenylsilyl−diphenylsilyl copolysilanes. Simple copolymers were employed to eliminate other factors associated with n and k values. The n and k values at 248 nm increase with increasing weight percentage of phenyl groups. A similar trend is shown for the relation-

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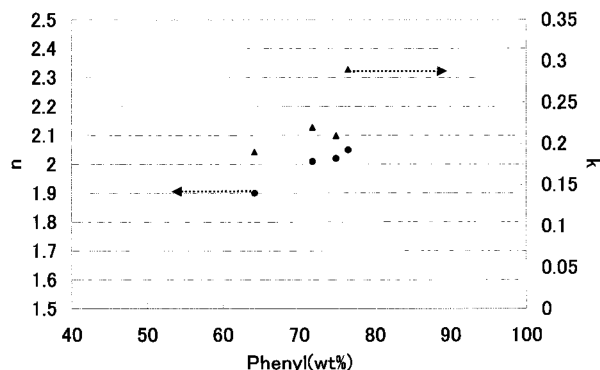

Figure 5. Relationship between percentage of phenyl groups and *n* and *k* values for methylphenylsilyl–diphenylsilyl copolymers.

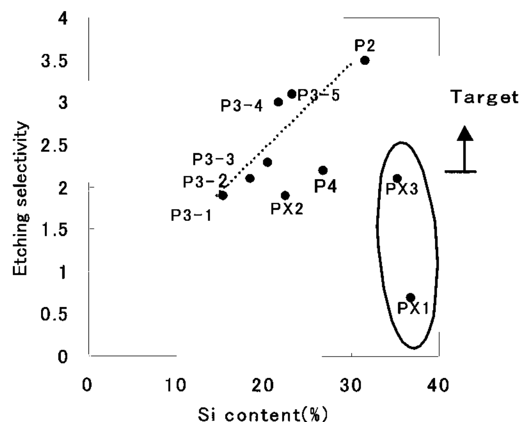

Figure 6. Relationship between silicon content and etching selectivity. Silicon content: wt %, Cl_2 gas. Selectivity: Etching rate of polysilane layer toward that of the resist layer (R1).

ship between the UV absorbance at 248 nm and the weight percentage of phenyl groups. A conventional resist has *n* and *k* values of 1.78 and 0.02, respectively. Therefore, the *n* value close to 1.78 and large *k* value should be suitable for low-reflection materials. Details of the reflection in device manufacturing have been reported elsewhere.[34]

In conclusion, the introduction of aromatic groups, the chain distortion, and the branching of the silicon main chain turned out to be effective for the increase in the UV absorption of the polysilane film at 248 nm.

3.2. Polysilane Etching Behaviors. 3.2.1. Relationship between Etching Selectivity toward Resists and Polysilane Structures. During etching of the polysilane layer by chlorine plasma, the polysilane layer must be etched anisotropically. The anisotropic etching conditions of polysilane films with a large aspect ratio have not been previously reported in detail. Fluorine-containing gases, Cl_2 gas, and HBr gas have been used for inorganic silicon etching.[51] The silicon layer is etched by chemical reactions and physical sputtering. The latter may contain chemical reactions assisted with ion bombardments.[51] The chemical reaction tends to etch the silicon layer isotropically while the physical sputtering tends to etch it anisotropically.[52]

It has been reported that fluorine-containing gases etch silicon layers isotropically because atomic fluorine in the plasma reacts with the silicon layer spontaneously. On the other hand, the process using Cl_2 and HBr gases provides anisotropic etching because spontaneous reactions of these gases with the silicon layer are very few and the etching occurs in the presence of ion bombardments. The difference between fluorine and chlorine gases has been explained by the boiling point of silicon halides and the ease with which the atomic halides can penetrate the silicon surface.[52] The boiling point of SiF_4 is 178 K and is particularly volatile, while $SiCl_4$ and $SiBr_4$ have boiling points of 330 and 427 K, respectively. Therefore, $SiCl_4$ and $SiBr_4$ are less desorbed from the silicon surfaces: their desorption is accelerated by bombardment with ions which attack the silicon surfaces anisotropically with the aid of a self-bias potential. The isotropic etching observed for fluorine gas has also been explained by the small size of the fluorine atom, 0.7 Å, making it possible to penetrate 10–20 Å in depth from the silicon surface. The covalent radius of Br is 1.1 Å and is comparable in size to a silicon atom (1.2 Å).[53–55] Therefore, in this study, Cl_2 gas was employed for the anisotropic etching of polysilane layers.

Figure 6 shows the relationship between the silicon content in the polymer and the etching selectivity of the polysilane toward the resist (R1). The etching selectivity increased with increasing silicon content for linear polysilanes having methyl and phenyl groups, such as P3–1, P3–2, P3–3, P3–4, P3–5, and P2.

The etching selectivity of polysilanes partially cross-linked at the ethylene unit, such as PX1, PX2, and PX3, was not as large as that for copolymers composed of linear polysilanes with comparative silicon content. From the relationship shown in Figure 6, P4 can be seen to lie below the line of the linear copolymers. This can be explained by the highly branched nature of the silicon atoms.

A significantly large deviation was observed for PX1 and PX3. They contain a propyl group and a bulky trimethylsilyl group. The etching selectivity for PX4, having a cyclohexyl and a naphthyl group, was also much less than that for PX1, not shown in Figure 6 because the etching condition was slightly different from the others shown in Figure 6. This also supports the fact that alkyl substituents longer than a methyl group decrease the etching selectivity.

Highly branched silicon backbones or cross-linking through the ethylene group increased the T_g of the polysilane. This increase in the T_g is needed to prevent the polysilane from being deformed thermally during the reactive ion etching. For example, the T_g of 128 °C for P3–2 increased to 155 °C for PX2 by the introduction of partial cross-linking by the ethylene group. Although the introduction of the cross-linking decreased the etching selectivity, the decrease was much less than that brought about by the introduction of large alkyl groups. Large or bulky alkyl groups should therefore be avoided. As far as etching selectivity is concerned, methyl groups would be the best choice; however, phenyl groups are

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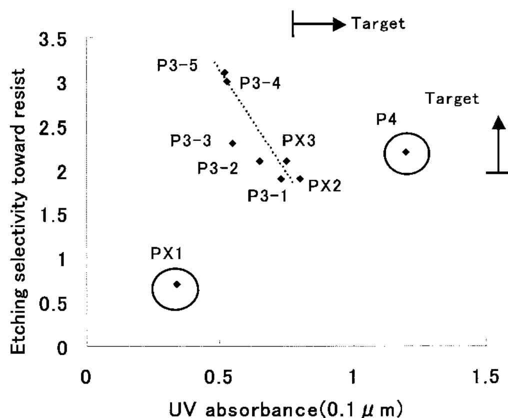

Figure 7. Relationship between etching selectivity toward resist and UV absorbance. Etching selectivity: see Figure 6. UV absorbance: see Figure 4.

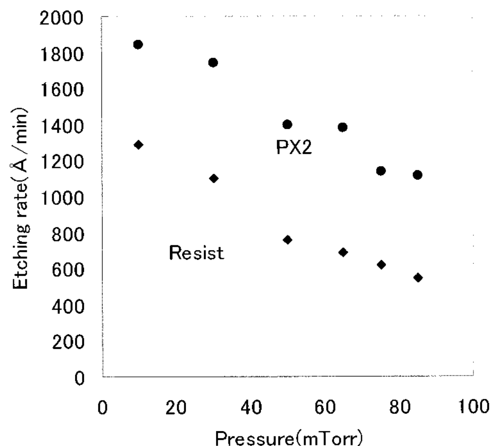

Figure 8. Relationship between etching rate and pressure in a chamber of Cl_2 gas.

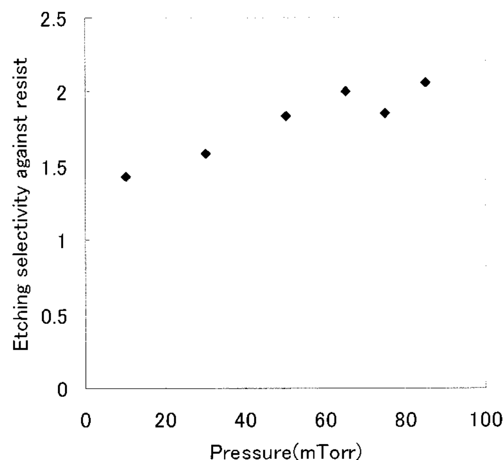

Figure 9. Relationship between etching rate and pressure in a chamber of Cl_2 gas. Etching selectivity: etching rate for PX2 toward resist RI.

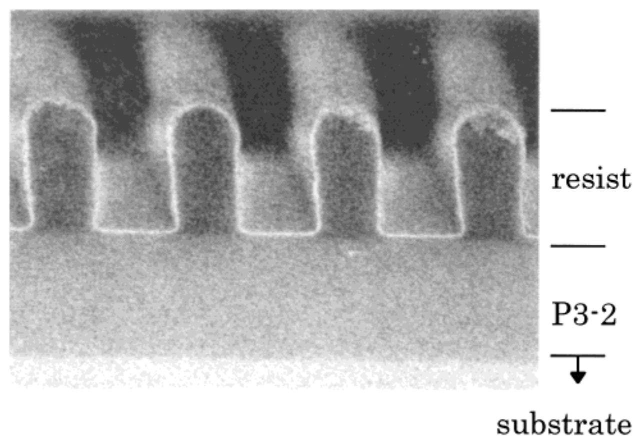

Figure 10. Resist patterns on polysilane antireflective layers before etching. Exposure: see Experimental Section. 0.2-μm L/S. Development: 2.38% tetramethylammonium hydroxide aqueous solution.

needed to make the polymers soluble in organic solvents and to fabricate uniform films.

Figure 7 shows the relationship between etching selectivity toward the resist and UV absorbance at 248 nm. If polysilanes have linear structures and are substituted with methyl and phenyl groups, the etching selectivity increases and the UV absorbance decreases with an increase in the silicon content. Therefore, it is difficult to find a linear polysilane structure with both a high etching selectivity and high UV absorbance. UV absorption groups, except for phenyl groups, have to be incorporated into the polysilane structure to satisfy the high etching selectivity and high UV absorption criteria. Highly branched polysilanes, such as P4, are one such candidate.

The presence of oxygen atoms in the polysilane structure was found to be crucial. Oxidation may occur during synthesis. In the case of P1 containing hydrogen groups, oxidation also occurs while the film is baked unless this process is carried out under argon. The etching selectivity for P1 decreased to 80% when 60% of Si–Si bonds was oxidized to Si–O–Si bonds and decreased to 40% when all of the Si–Si bonds were oxidized. P1 has Si–H groups and is easily oxidized. The oxidation was monitored by the IR absorption of Si–O–Si bonds versus that of Si–Ph bonds. The difference in the etching rate between oligosilanes and oligosiloxanes will be discussed using a MO calculation, later. The oxidation of polysilanes should be avoided during their synthesis and the film preparation.

3.2.2. Effects of Pressures in an Etching Chamber. Figure 8 shows the relation between the pressure in an etching chamber and the etching rate of the PX-3 film toward the resist film, R1. As ion energies are lowered by surrounding molecules, it is expected that at lower pressures etching will be dominated by physical processes, while the etching at higher pressures emphasizes chemical processes.[52] The etching rate for the resist film R1 and the PX-3 film decreased with increasing pressure. However, the etching selectivity of the PX3 film against the resist film R1 increased with an increase in the pressure as shown in Figure 9. This implies that the etching behavior of the PX-3 film is similar to that for the organic resist R1 but the etching of the PX-3 film is a little more pronounced as a result of the chemical reaction, probably because Si–Si bonds are more chemically reactive than C–C bonds.

Figure 10 shows the resist R1 pattern fabricated on the polysilane antireflective layer, P3–2. Standing waves caused by reflections were not observed in the wall of the R1 pattern. Figure 11 shows the polysilane pattern after the polysilane layer was etched by Cl_2 plasma. The pattern had vertical walls, leading to the

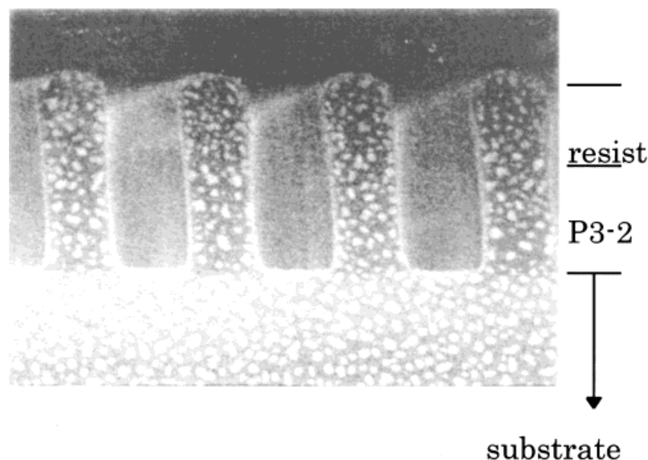

Figure 11. Resist and polysilane patterns after etching. Resist thickness, 0.3 μm; polysilane thickness, 0.3 μm, 0.2 μm L/S. Etching: Cl_2 gas.

conclusion that etching was conducted anisotropically.

3.3. Reaction Mechanism. Etching rates of silicon substrates by Cl_2 gas have been discussed in terms of their reactivity with chlorine radicals, the volatility of reaction products, their reactivity toward radicals assisted by ion bombardments, and physical sputtering.[52] The physical sputtering is affected mainly by the film density. The film density of polysilane films was almost the same as that of the organic resist film R1, namely, 1.2−1.4 g/cm^3. Therefore, we assumed that the etching of polysilane films by physical sputtering should be almost the same as that for the resist R1.

The etching results were discussed in terms of the reactivity with chlorine radicals and the volatility of reaction products.

3.3.1. Reactivity of Polysilanes with Chlorine Radicals. Polysilanes have Si−Si, Si−C, and C−C bonds, among which Si−C and Si−Si bonds are characteristic to polysilanes.

To elucidate the etching mechanism, the polysilane surface was analyzed by X-ray photoelectron spectroscopy (XPS). Figure 12 shows Si 2p photoelectron spectra of P3−5 before and after Cl_2 etching. The P3−5 film has a peak at 101 eV assigned to the polysilane main chain silicon atoms (Figure 12 a). The value seems to be a little higher than 100.5 and 99.5 eV reported for poly(phenylalkyl)silanes and polysilylenes, respectively.[56,57] The P3−5 may contain a small amount of Si−O bonds. When the P3−5 film was exposed to Cl_2 gas, the peak did not change (Figure 12 b). The peak shifted to 103 eV and became broader after the P3−5 film was exposed to Cl_2 plasma (Figure 12 c). The shift in the binding energy due to one Si−Cl has been estimated to be about 1.1 eV.[51] Therefore, the peak shift of about 2 eV and peaks overlapped with broad peaks in the lower energy region could be assigned to silicon atoms bearing a few Cl groups.[52] We are not able to exclude the possibility that the peak may contain components attributed to Si−O linkages that should be formed as a result of the reaction of Si−Cl with H_2O. A similar peak shift has

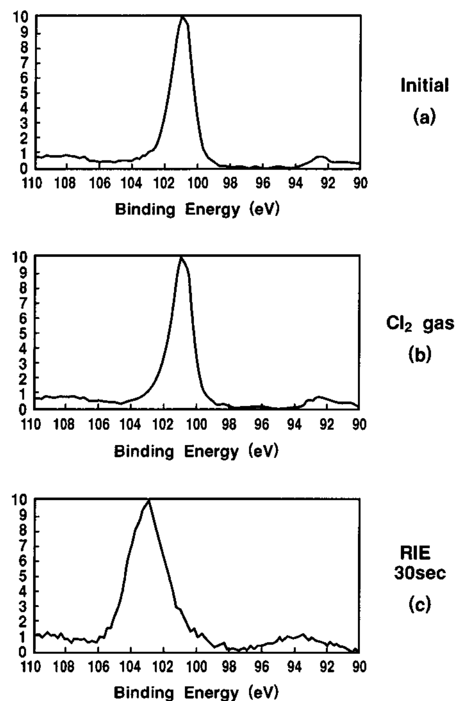

Figure 12. Si 2p XPS before and after Cl_2 plasma exposures for P3−5 film. (a) initial, (b) polysilane film exposed to Cl_2 gas, and (c) polysilane film exposed to Cl_2 gas plasma for 30 s.

been observed previously in the case of fluorine and HBr-etched silicon surfaces when silicon−fluorine species and silicon−bromine species were formed.[59−62] Actually, $SiCl_4$ gas was detected by mass spectroscopy (MS) in the exhaust gases from the etching chamber. At this stage, the other decomposition products had not been detected. Further investigation of the compositions of the exhaust gases is needed to clarify the reaction mechanism.

3.3.2. MO Calculations. Etching behaviors observed in Figures 6−9 were explained tentatively using MO calculation (Figures 13 and 14). There are many possible mechanisms that adequately account for the decomposition of oligosilanes to small molecules during etching. For clarity and simplification only one pathway will be considered here. WinMopac V1.0, PM3 was used to calculate the heat of formation for each material in the reaction sequence. The activation energies for various reactions should be taken into account. However, tentatively, we used the difference in the heat of formations on the assumption that radical reactions have low activation energies. Steric hindrance may increase the activation energy; however, the trend in the change of steric hindrance should be the same between silicon-based and carbon-based polymer model compounds. Therefore, the relative ease of the reaction can be compared by considering the change in the heat of formation between the two model compounds.

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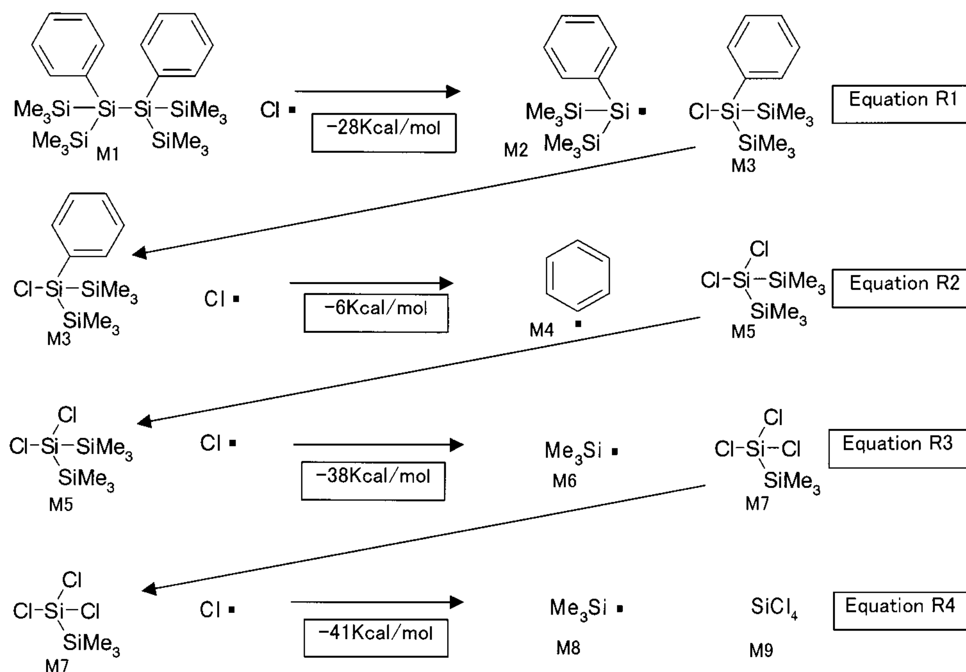


Figure 13. Difference in heat of formation of polysilane model compounds. The values were obtained by subtracting the heat of formation of starting materials from that of reaction products. Negative values mean that reaction products are thermodynamically stable compared to starting materials.

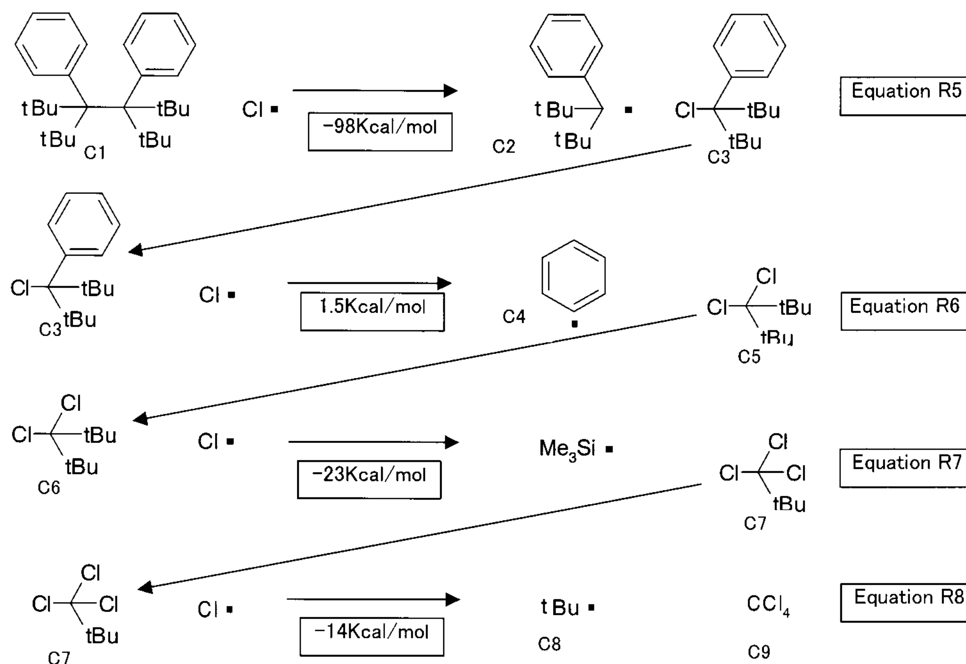
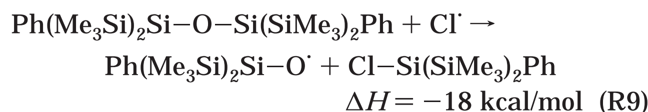


Figure 14. Difference in heat of formation of organic resist model compounds. Explanation: see Figure 13.

The values in Figure 13 were obtained by subtracting the heat of formation of the starting materials from those of the reaction products. Therefore, negative values mean that the reaction product is thermodynamically stable compared to the starting material. For example, the difference in the heat of formation was −28 kcal/mol when M−1, a model polysilane compound, reacted with a Cl radical to form the silyl radical (M2) and the silyl chloride (M3). It is expected that the reaction giving a large negative value will proceed preferably. Because of the inaccuracy of these absolute values for the heat of formation, we will discuss them only in relative terms. In the case of M1, the difference in the heat of formation increased in the order of equations R1, R3, and R4. Figure 13 shows the results of the carbon compound (C1) in which the silicon atoms in M1 are replaced with carbon atoms. In the case of C1, the difference in the heat of formation increased in the order of equations R8, R7, and R5. In the case of silicon compounds, as decomposition proceeds and the substituents on the silicon atom are replaced with Cl groups, decomposition occurs more readily. However, in the case of carbon compounds, the trend was opposite. This result explains well the observation that polysilanes are etched faster than organic polymers by Cl plasma gases.

The difference in the heat of formation in eq R2 was −6 kcal/mol, which is smaller than that in eqs R1, R3, and R4. This implies that the cleavage of Si−Si bonds occurs more easily than that of Si−C bonds. An increase in the amount of Si−Si bonds is needed to increase the etching selectivity toward resists, which is consistent with the results obtained in Figure 6.

The effect of oxygen atoms in the polysilane film on the etching selectivity was also considered. MO1, $Ph(Me_3Si)_2Si{-}O{-}Si(SiMe_3)_2Ph$, was employed as a model compound for oxidized polysilanes. The difference in the heat of formation in eq R9 was calculated to be −18 kcal/mol, which is energetically unfavorable by 10 kcal/mol to that for the reaction of M1 with chloride radicals (eq R1). The calculation also showed the etching selectivity of the oxidized polysilane to be smaller than that of the unoxidized polysilane film.



$$Ph(Me_3Si)_2Si{-}O{-}Si(SiMe_3)_2Ph + Cl^{\cdot} \rightarrow Ph(Me_3Si)_2Si{-}O^{\cdot} + Cl{-}Si(SiMe_3)_2Ph \quad \Delta H = -18 \text{ kcal/mol} \quad (R9)$$

3.3.3. Volatilities of Reaction Products. Reaction products have to be removed from film surfaces swiftly to promote dry etchings. Therefore, the volatility of reaction products has been reported to be one of the factors determining the dry etching rates.[52] When P3−2 is exposed to chlorine plasmas, a number of small molecules containing one silicon atom, for example, tetrachlorosilane (Si1), methyltrichlorosilane (Si2), phenyltrichlorosilane (Si3), and methylphenyldichlorosilane (Si4), can result. Their boiling points are 57, 66, and 80 °C/10 mmHg and 55 °C/1 mmHg, respectively. Because etchings were carried out at 80 °C under reduced pressure, Si1 and Si2 would be removed effectively. Si3 and Si4 may need further bond cleavages for volatilization. The boiling point of propyltrichlorosilane (Si5), which is characteristic of PX1 decomposition, is 123 °C. This is higher than that of Si2 containing a methyl group. This may partially explain the phenomena that the etching rate for polysilanes bearing a propyl or cyclohexyl group is extremely low. In addition, this phenomena may be explained by the fact that long alkyl groups bonded to polysilane backbones are easily cross-linked by ion attacks, resulting in nonvolatility. For poly(di-*n*-hexylsilane), cross-linking had been reported to occur by ion beam irradiation, containing H^+, He^+, and He^{2+} ions.[63]

4. Conclusions

UV absorption of polysilanes at 248 nm increased with an increasing number of phenyl groups substituted on the silicon atoms and the extent of branching of the silicon backbone. The etching selectivity of polysilanes toward organic resists increased with an increase in the amount of silicon atoms in polysilane films. However, the introduction of alkyl groups longer than methyl groups decreased the selectivity. Highly branched polysilanes are a potential candidate for satisfying both the high etching selectivity and the high UV absorption at 248 nm. The phenomena that polysilanes are etched more rapidly than organic resists by Cl_2 plasma were explained in terms of the higher chemical reactivity of Si−Si bonds with chloride radicals, higher volatilities of these reaction products. It was proved that polysilane layers prevented reflections from the substrate and were etched anisotropically to give patterns with vertical walls.

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