

Si-H Group Elimination Effect on the Properties of SiOCH Films: Theoretical Investigation

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1. Introduction

Materials with lower dielectric constants (low- k) are needed for the intermetal dielectrics of future silicon devices. The most promising candidate material for the low- k dielectrics currently is the SiOCH film, but the conventional SiOCH films of smaller k -value are less compatible to the device integration because of the smaller mechanical strengths. We therefore have to find appropriate chemical group modifications of SiOCH films to achieve both high mechanical strength and low dielectric constant.

To obtain the guidelines to produce films of appropriate chemical structure, we have been studying the film-property dependence on the component chemical groups of SiOCH films by theoretical calculations [1]. In the present study, we focus on the films having Si-H groups. The Si-H group is one of the typical chemical groups of the SiOCH low- k films, but actually only little is known concerning how this chemical group affects the film properties. In our recent experimental study [2], a PECVD-SiOCH film of excellent quality ($k = 2.37$, Young's Modulus (E_Y) = 8GPa) could be deposited using DCPDMOS precursor (Fig.1) by eliminating the Si-H groups. The experimental data (Fig.2) suggest that the Si-H group elimination has positive effect for decreasing the dielectric constants of SiOCH films, although this effect includes the influence from the other chemical components. In the following sections, the importance of Si-H group elimination for the property improvement of SiOCH films is investigated theoretically.

2. Si-H group and dielectric property of SiOCH films

The dielectric properties of the Si-H group and other typical chemical groups of SiOCH films have been compared first. The chemical group substitution effect has been examined computationally using a small siloxane molecule model for this analysis. The molecules examined are cyclic siloxanes $\text{Si}_4\text{O}_5\text{H}_4\text{X}$ (Fig.3), where the Si-X-Si part is replaced with 2(Si-H) and the other well-known chemical groups of SiOCH films such as 2(Si-CH₃), 2(Si-OH), and Si-O-Si. Note that we should focus on the relative polarizabilities (α) and volumes (V) of these molecules here, since the atom groups affect the dielectric constant of molecules/materials through these two properties (dielectric constant is defined as $k = (\alpha/V)/\epsilon_0$

+ 1). The properties of these molecules have been calculated by the density functional theory (B3LYP functional [3]) with the aug-cc-pVDZ [4] basis set using the Gaussian 03 program [5].

The calculated polarizabilities (α) of these molecules are shown in Table 1, with the contributions from the electronic and the ionic polarizations (α_{elec} and α_{ion} , respectively). The data indicates that the Si-H groups make siloxane molecules less polarizable than the Si-CH₃ groups and the Si-OH groups, while more polarizable than the Si-O-Si group. The smaller polarizability of $\text{Si}_4\text{O}_5\text{H}_4(\text{H})_2$ than that of $\text{Si}_4\text{O}_5\text{H}_4(\text{CH}_3)_2$ results mainly from the electronic contributions, which should be ascribed to the different HOMO-LUMO gaps of these molecules (7.99 eV and 7.72 eV, respectively), while the smaller polarizability of $\text{Si}_4\text{O}_5\text{H}_4(\text{H})_2$ than that of $\text{Si}_4\text{O}_5\text{H}_4(\text{OH})_2$ results mainly from the ionic components, which should be ascribed to the different polarities of the Si-H group and the Si-OH group. The electronic and ionic components contribute almost evenly for the larger polarizability of $\text{Si}_4\text{O}_5\text{H}_4(\text{H})_2$ than that of $\text{Si}_4\text{O}_5\text{H}_4(\text{O})$. The larger ionic polarizability of $\text{Si}_4\text{O}_5\text{H}_4(\text{H})_2$ than that of $\text{Si}_4\text{O}_5\text{H}_4(\text{O})$ means that the Si-H groups make this molecule more deformable than the cross-link Si-O-Si.

The calculated volumes of these molecules (Table 1) indicate that the Si-H groups make siloxane molecule smaller than the Si-CH₃ groups and the Si-OH groups, while larger than the Si-O-Si group.

If the calculated chemical group dependences of the polarizability and the volume are applicable to siloxane compounds generally, we can discuss the influence of atom group substitutions on the k -value of typical SiOCH films ($k \sim 3$, electric susceptibility $\alpha/V = (k - 1) \epsilon_0 \sim 2.0 \epsilon_0$), as follows. i) The substitution Si-H $\rightarrow$ Si-CH₃ would decrease the k -value of the SiOCH films, because this substitution increases both α and V , and the ratio of the changes $\Delta\alpha/\Delta V = 0.95 \epsilon_0$ is smaller than the electric susceptibility of typical SiOCH film of $\sim 2.0 \epsilon_0$ ii) The substitution Si-H $\rightarrow$ Si-OH would not change the k -value of SiOCH film so much, because the ratio of the changes $\Delta\alpha/\Delta V = 1.84 \epsilon_0$ is comparable to $2.0 \epsilon_0$. iii) The substitution 2(Si-H) $\rightarrow$ Si-O-Si would decrease the k -value of SiOCH film, because this substitution decreases both α and V , and the ratio of the changes $\Delta\alpha/\Delta V = 4.57 \epsilon_0$ is larger than $2.0 \epsilon_0$, meaning steep decrease of α against V . These analyses suggest that

the Si-H bond is not a favorable chemical group for decreasing the dielectric constant of SiOCH films.

3. Si-H group and the mechanical property of SiOCH films

The chemical group substitution effect on the mechanical property of the SiOCH film has been examined using three-dimensionally periodic polymer models. We have compared hypothetical model structures $\text{Si}_{20}(\text{-O-})_{25}(\text{-H})_{30}$, $\text{Si}_{20}(\text{-O-})_{30}(\text{-H})_{20}$, and $\text{Si}_{20}(\text{-O-})_{25}(\text{-H})_{20}(\text{-CH}_3)_{10}$ for this analysis, where ten of the Si-H groups of the first model structure are replaced with the Si-O-Si groups and the Si-CH₃ groups in the second and third model structures, respectively. The Young's moduli (the measure of the mechanical strengths) of these model structures are calculated by classical constant pressure molecular dynamics (MD) simulations. The dielectric constants of these structures have been calculated also since our concern is not only on the mechanical strength but on the balance of the mechanical strength with the dielectric constant. See ref. 6 for the methods of model structure creation and the dielectric constant calculation of the polymer model structures.

The calculated results for $\text{Si}_{20}(\text{-O-})_{25}(\text{-H})_{30}$, $\text{Si}_{20}(\text{-O-})_{30}(\text{-H})_{20}$ are shown in Fig. 4. The model structures of $\text{Si}_{20}(\text{-O-})_{30}(\text{-H})_{20}$ have larger Young's Modulus than the model structures of $\text{Si}_{20}(\text{-O-})_{25}(\text{-H})_{30}$, which is naturally understandable since the atoms in the former model structures are more firmly bound by more oxygen cross-links than in the latter. The point of this data is that the former model structures keep certain Young's modulus at lower k -value than the latter. This result means that eliminating the Si-H groups of SiOCH films is a way to create high-modulus and low- k films, if accompanied by the increase of oxygen cross-links. The figure suggests that the mechanical strengthening is more essential than the k -value decrease in this Si-H group elimination effect.

The calculated results for the $\text{Si}_{20}(\text{-O-})_{25}(\text{-H})_{20}(\text{-CH}_3)_{10}$ will be presented at the conference.

4. Summary

It has been suggested from the theoretical calculations that the Si-H bond is not a favorable chemical group for decreasing the dielectric constant of SiOCH films. It has been suggested that eliminating Si-H bonds is an effective way to obtain high-modulus and low- k SiOCH films, if accompanied by the increase of oxygen cross-links.

References

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Fig. 1. Chemical structure of DCPDMOS. (dicyclopentyl-dimethoxy-silane)

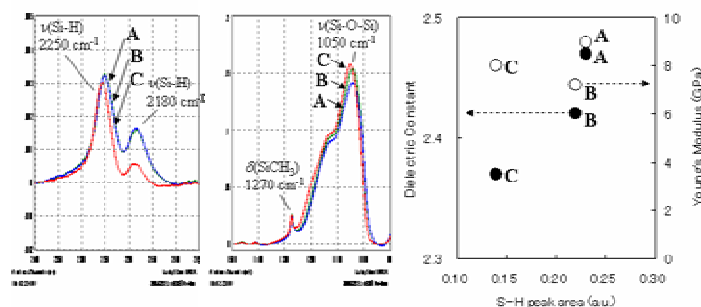
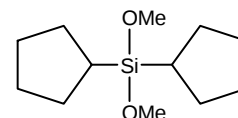


Fig. 2. Infrared spectra (frequency regions 2050-2400 cm⁻¹ (left) and 900-1500 cm⁻¹ (right)) and properties (filled circle: dielectric constant, open circle: Young's modulus) of SiOCH films deposited from the DCPDMOS precursor under various experimental conditions. Densities of films A-C: 1.16 g/cm³, 1.14 g/cm³, and 1.14 g/cm³, respectively.

Fig. 3. Chemical structure of the cyclic siloxane $\text{Si}_4\text{O}_5\text{H}_4\text{X}$.

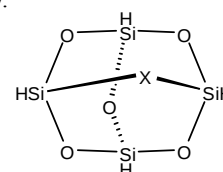


Table 1. Molecular polarizability (α) and volume (V) of the cyclic siloxane $\text{Si}_4\text{O}_5\text{H}_4\text{X}$,^a calculated at B3LYP/aug-cc-pVDZ.

		Si-X-Si			
		2(Si-H)	2(Si-CH ₃)	2(Si-OH)	(Si-O-Si)
α_{elec}	(a.u.) ^b	101.6	126.5	105.8	94.4
α_{ion}	(a.u.) ^b	51.3	61.8	72.0	41.6
α_{total}	(a.u.)	152.9	188.2	177.8	136.0
V	(bohr ³)	1840.7	2310.6	2010.6	1794.4
$\Delta\alpha_{\text{total}}$	(a.u.) ^c	-	35.4	24.9	-16.8
ΔV	(bohr ³) ^c	-	470.0	169.9	-46.3
$\Delta\alpha_{\text{total}}/\Delta V$	(ϵ_0)	-	0.95	1.84	4.57

^a See Fig.3 for the molecular structure of $\text{Si}_4\text{O}_5\text{H}_4\text{X}$. ^b Contribution from the electronic polarization α_{elec} and that from the ionic polarization α_{ion} . ^c Relative values from the data for 2(Si-H).

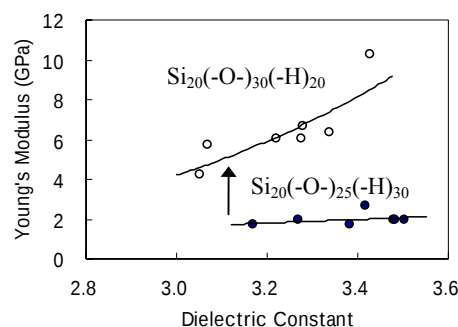


Fig. 4. Young's moduli and dielectric constants of the film model structures $\text{Si}_{20}(\text{-O-})_{25}(\text{-H})_{30}$ and $\text{Si}_{20}(\text{-O-})_{30}(\text{-H})_{20}$. Plural data points for respective model structures represent the isomers with different cross-link topologies or different 3D atom arrangements.